# Coatings on Earth and Beyond

**The Coatings Summit 2015**

Shaping the Future of a Dynamic Industry

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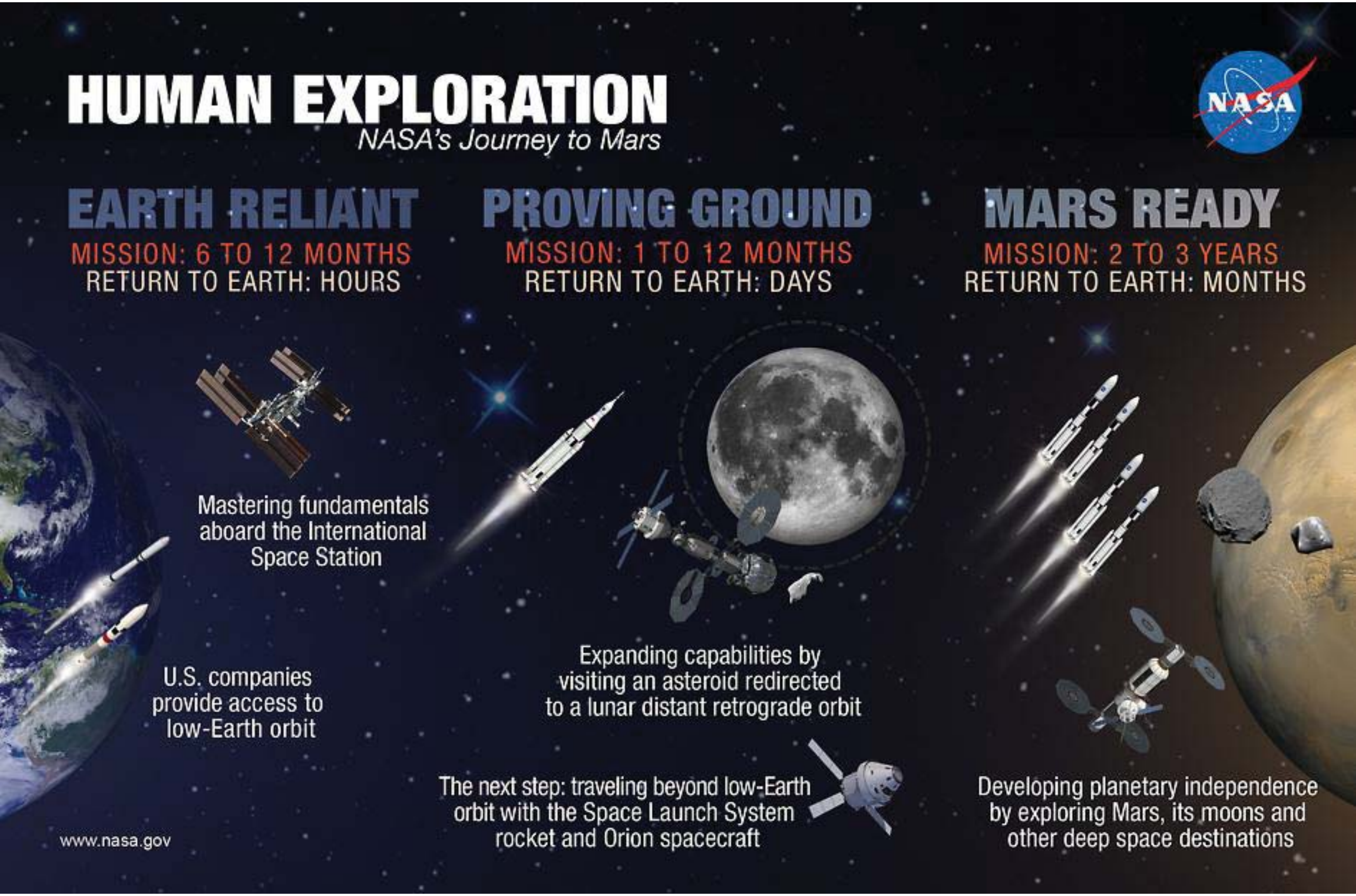
**Kennedy Space Center, FL, 32899, USA**

# Outline

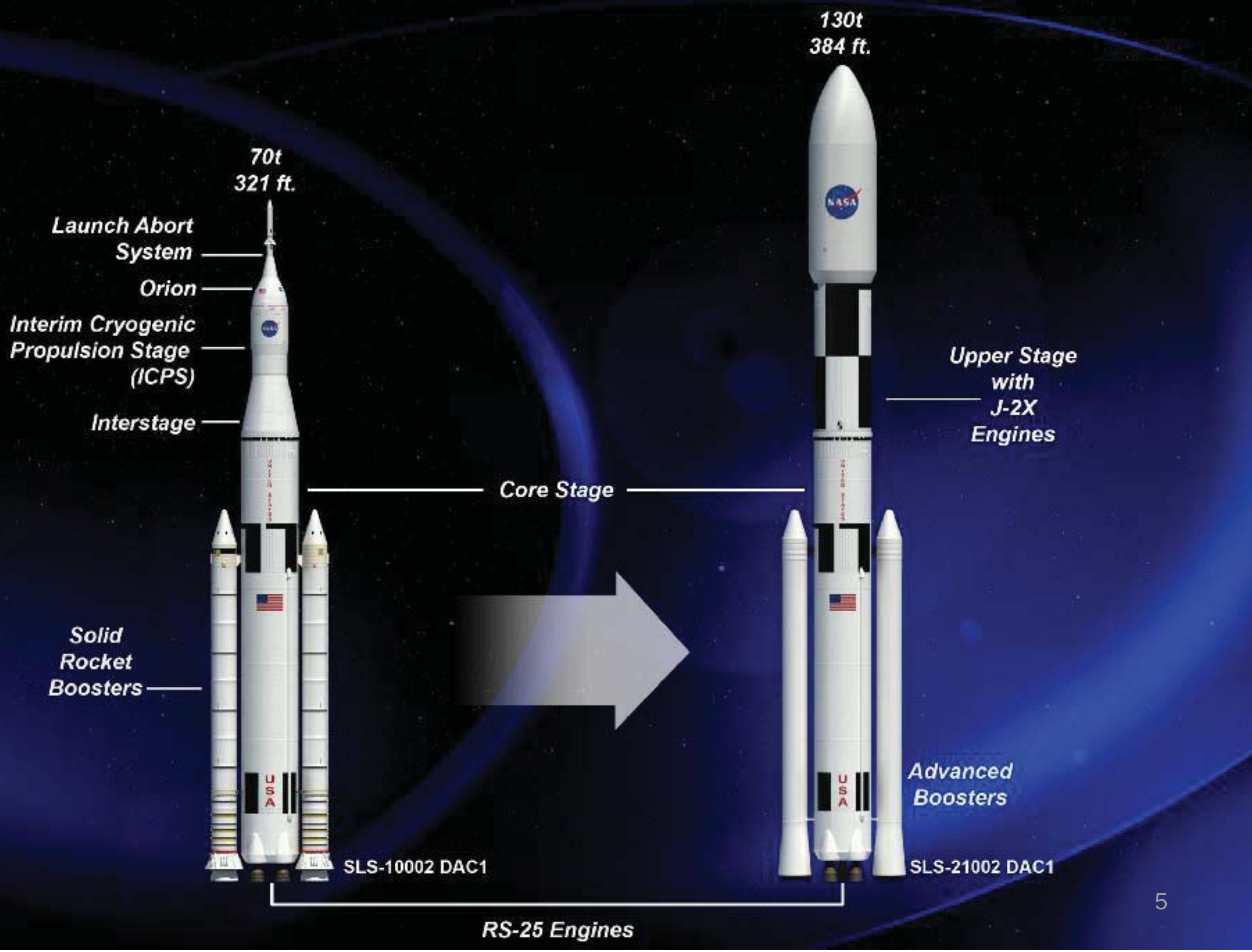
- What is NASA doing and why are coatings on earth and beyond important to NASA?
- Corrosion
  - Definition and impact
  - Coatings for the space environment
  - Natural and Launch environments at NASA's Kennedy Space Center (KSC)
  - Corrosion at KSC
  - Cost of corrosion (worldwide and at KSC)
  - Corrosion grand challenges
  - Corrosion challenges at KSC timeline
- Coatings evaluation at KSC
  - Historical timeline
  - Current
  - Environmentally driven projects
- Technology Development
  - New accelerated corrosion test method
  - Smart coatings

# What is NASA doing and Why are Coatings Important to NASA?

"NASA's Space Launch System (SLS) and Orion will allow human exploration to continue beyond the moon in ways that were once a glimmer in our minds eye. Now we are building the hardware and developing the engineering operations teams that will launch the vehicle that will one day take people to Mars"



HUMAN EXPLORATION
NASA's Journey to Mars
NASA
EARTH RELIANT
MISSION: 6 TO 12 MONTHS
RETURN TO EARTH: HOURS
PROVING GROUND
MISSION: 1 TO 12 MONTHS
RETURN TO EARTH: DAYS
MARS READY
MISSION: 2 TO 3 YEARS
RETURN TO EARTH: MONTHS
Mastering fundamentals aboard the International Space Station
U.S. companies provide access to low-Earth orbit
Expanding capabilities by visiting an asteroid redirected to a lunar distant retrograde orbit
The next step: traveling beyond low-Earth orbit with the Space Launch System rocket and Orion spacecraft
Developing planetary independence by exploring Mars, its moons and other deep space destinations
www.nasa.gov

# SLS Architecture Reference Configuration



# What is Corrosion?

- Corrosion is the deterioration of a material due to reaction with its environment (M.G. Fontana). It literally means to "gnaw away"
- Degradation implies deterioration of the properties of the material.

KSC Launch Pad Corrosion (after a Space Shuttle launch)

KSC Crawler/Transporter Structural Steel Corrosion

# Impact of Corrosion


Repairs will cost about $60 million USD and take about 2 years

*Research Opportunities in Science and Engineering, Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council, The National Academies Press, 2011*

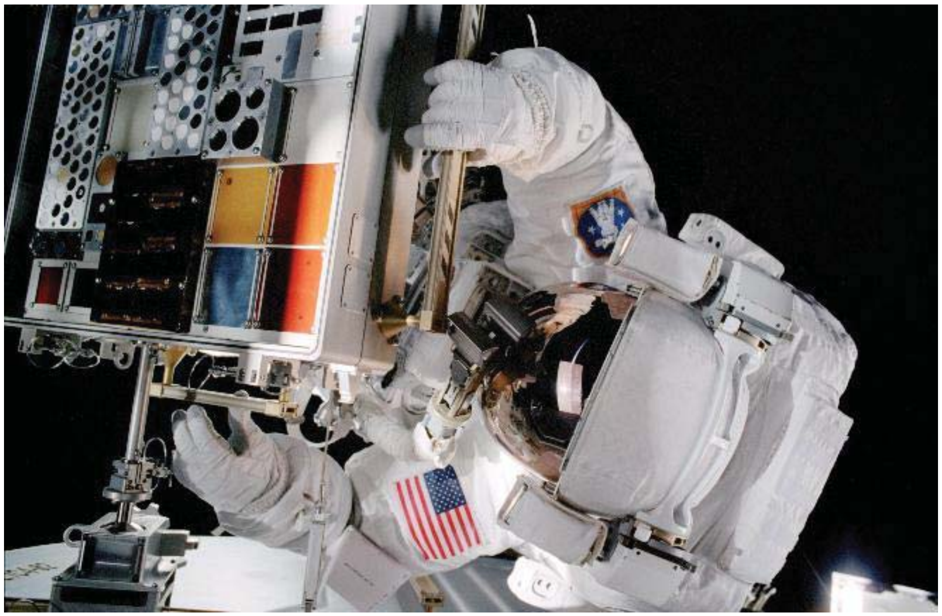
# Coatings for the Space Environment

The Space Environment is characterized by:

- Low pressure (vacuum)
- Atomic Oxygen (causes erosion of materials)
- Ultraviolet (UV) radiation
- Charged particles
- Temperature extremes
- Electromagnetic radiation
- Micrometeoroids
- Man-made debris

# Materials Testing for Space

Materials are tested on the exterior of the International Space Station. The payload container is mounted so one side faces the Earth and the other faces space. The experiments provide a better understanding of material durability, from coatings to electronic sensors, which could be applied to future spacecraft designs.



NASA astronaut Patrick G. Forrester installs exposure experiments designed to collect information on how different materials weather in the environment of space

NASA astronaut Andrew Feustel retrieves long duration materials exposure experiments before installing others during a spacewalk on May 20, 2011.

# Coatings on Orion Spacecraft

Corrosion protection coating on aluminum lithium alloy (left) and heat shield (right). The heat shield protects the spacecraft from temperatures reaching 4000 degrees Fahrenheit (2204 $^{o}$C)

# Orion Heat Shield

Textron technicians apply the Avcoat material by “gunning” the material into each of the 330,000 individual cells of the honeycomb structure

# Atomic Oxygen Restoration

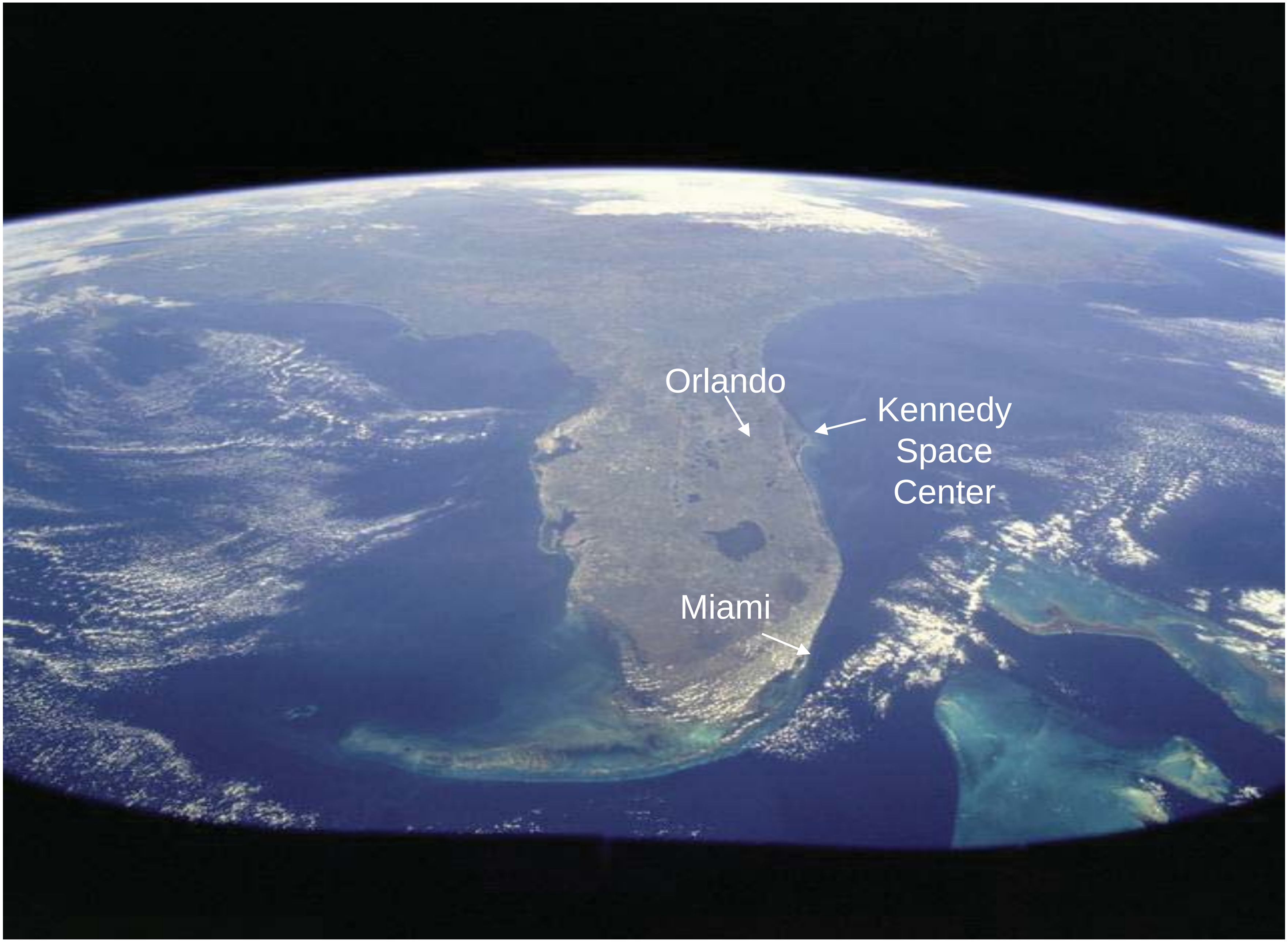
Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night (right photo), in part, due to atomic oxygen.

In the upper reaches of the atmosphere, about 200-500 miles, an elemental form of oxygen is created from exposure to intense solar ultraviolet light. Oxygen molecules are decomposed from $O_2$ into two separate oxygen atoms. This form of elemental oxygen is highly reactive and exposes a spacecraft to corrosion that shortens its life. While developing methods to prevent damage from atomic oxygen, it was discovered that it could also remove layers of soot or other organic material from a surface. Atomic oxygen will not react with oxides, so most paint pigments will not be affected by the reaction.

# International Space Station Technology – Benefits Fine Art

The left photo was taken after the Cleveland Museum of Art's staff attempted to clean and restore it using acetone and methylene chloride. The right photo is after cleaning by the atomic oxygen technique.

# Natural and Launch Environment at KSC




The Kennedy Space Center in Florida, USA, is a special place where we launch rockets from a wild life refuge in one of the most corrosive areas in the world
Rod Ostoski

# KSC Natural Environment

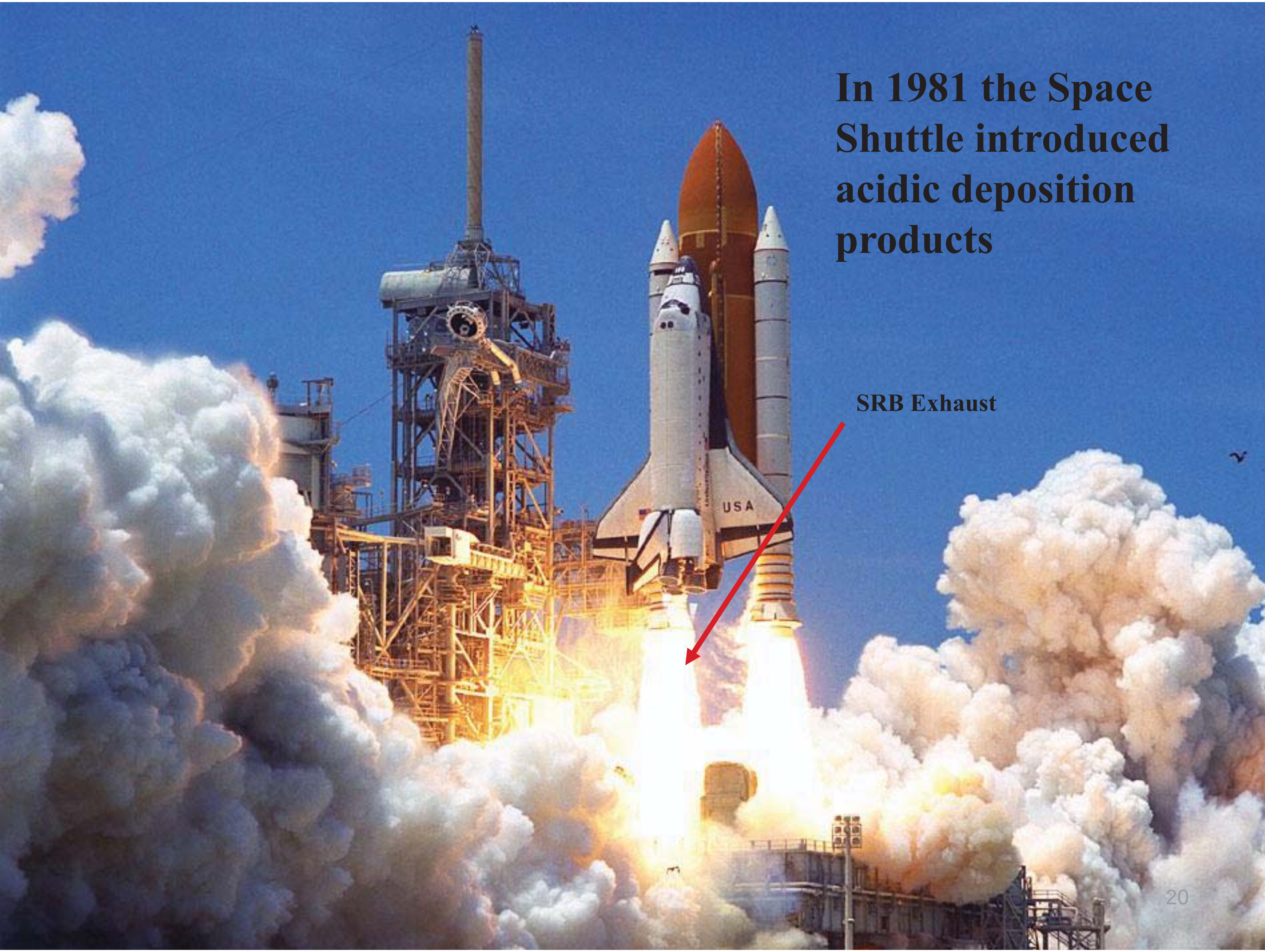
# KSC Natural Environment

# KSC Launch Environment

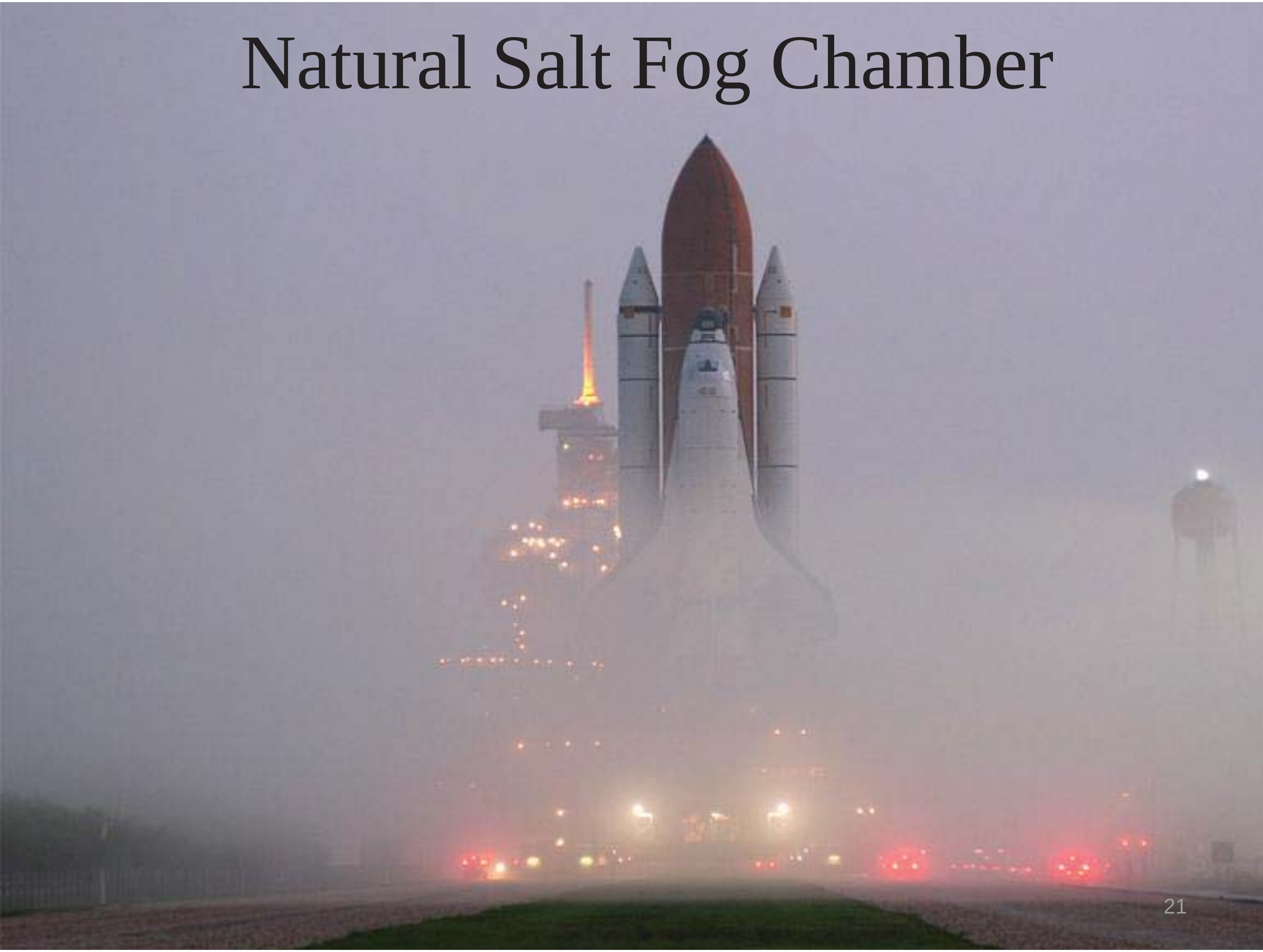
# KSC Launch Environment

The launch environment at KSC is extremely corrosive:

- Ocean salt spray
- Heat
- Humidity
- Sunlight
- Acidic exhaust from Solid Rocket Boosters (SRBs)


In 1981 the Space Shuttle introduced acidic deposition products
SRB Exhaust
USA

# Natural Salt Fog Chamber



# Examples of Launch Pad Corrosion

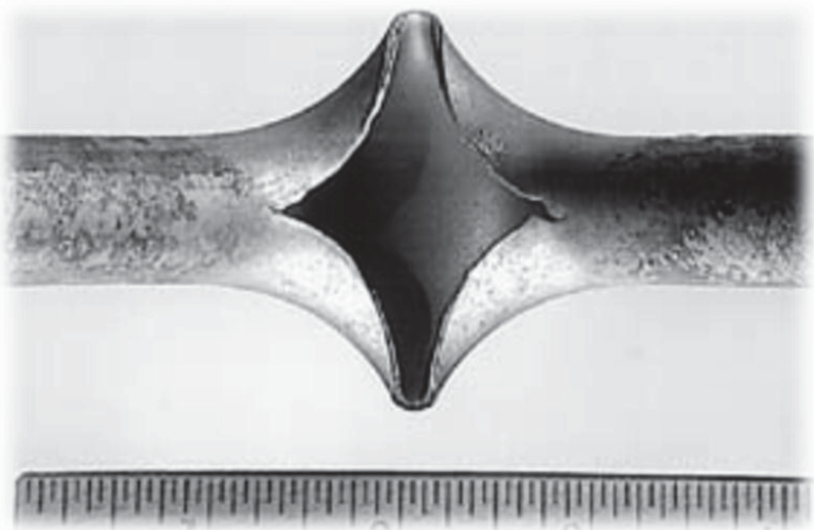
Enclosed / Inaccessible Areas

Dissimilar Metals


KSC Launch tower structural steel corrosion

Under the LC 39B Flame Trench

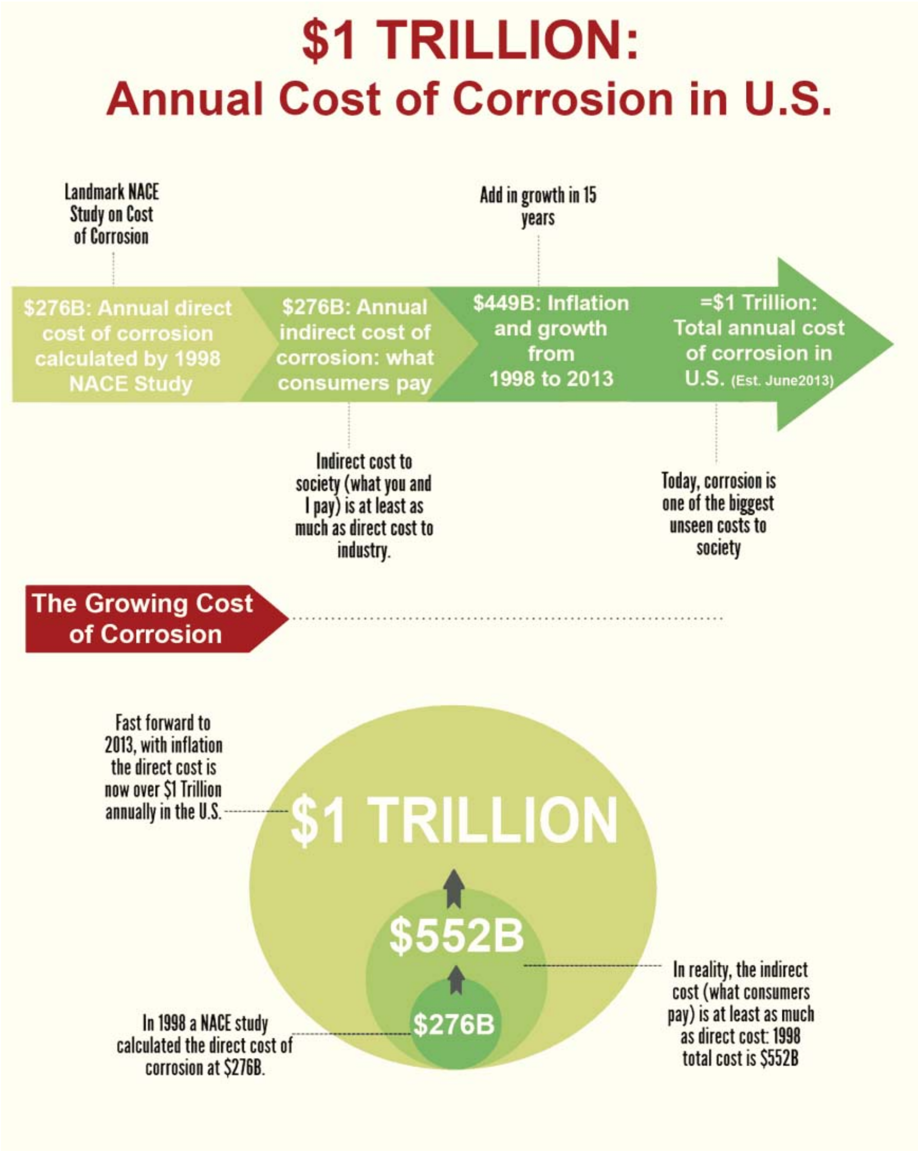
# Corrosion Failures



Tubing split caused by Pitting

Hidden corrosion

# Cost of Corrosion




- **At US $2.2 (1.6 €) trillion, the annual direct cost of corrosion worldwide is over 3% of the world's GDP.***
- **Direct costs do not include the environmental damage, waste of resources, loss of production, or personal injury.**

*World Corrosion Organization 2010

(1 Trillion = $10^{12}$ = 1 billon)

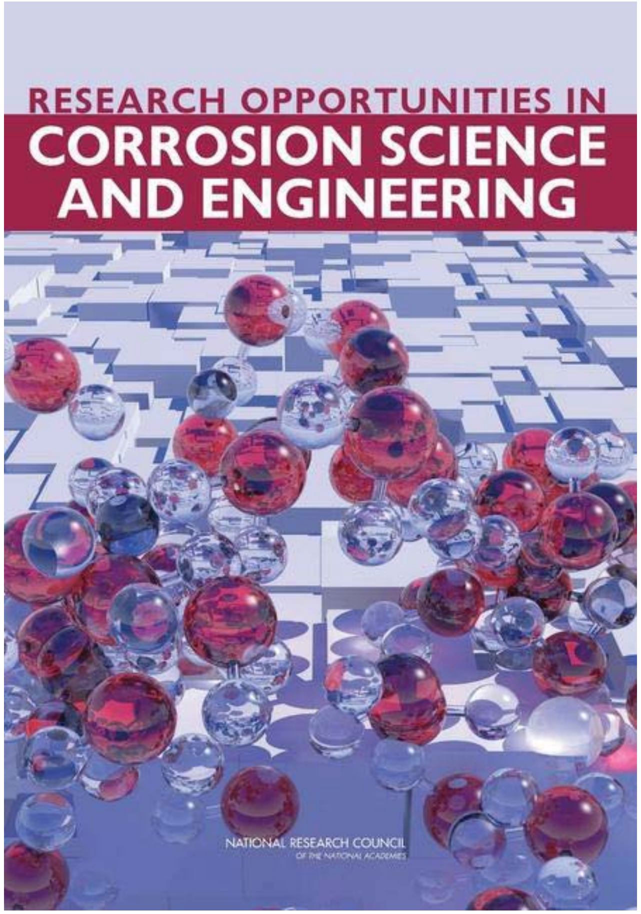
# Cost of Corrosion Control at KSC Launch Pads

## $1.6M/year[1]


[1] Estimate based on corrosion control cost of launch pads (39A and 39B) and the 3 Mobile Launch Platforms (MLPs) in 2001

# Corrosion Grand Challenges*

- Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings.
- High-fidelity modeling for the prediction of corrosion degradation in actual service environments.
- Accelerated corrosion testing under controlled laboratory conditions. Such testing would quantitatively correlate with the long-term behavior observed in service environments.
- Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary. i.e., corrosion prognosis.




***Research Opportunities in Corrosion Science and Engineering,** Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council (2010)

# Corrosion Challenges at KSC Timeline

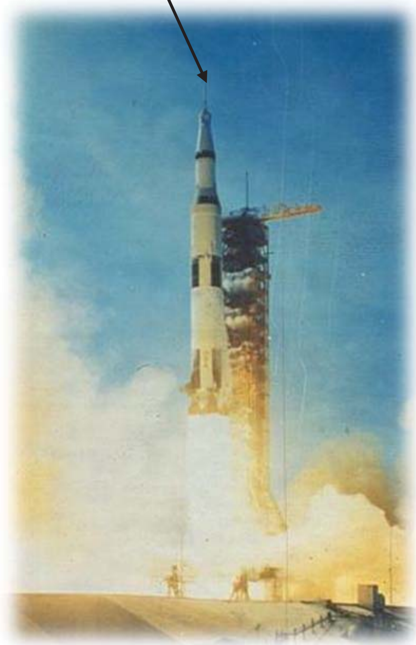
| 1962 | 1966 | 1981 | 1985-1987 | 2000 | 2004 |
|---|---|---|---|---|---|
| Space Program starts<br><br>Corrosion failures begin | Atmospheric exposure testing begins near the launch pads | Space Shuttle introduces acid deposition products that make corrosion worse | Accelerated corrosion testing (salt fog and electrochemical) begins | Corrosion Technology Laboratory is created | The Corrosion Technology Laboratory starts developing smart coatings |


Corrosion testing and failure analysis

Corrosion testing and technical innovation

# Coating Evaluation Studies at KSC

- Coating evaluation studies at KSC began in 1966 during the Gemini/Apollo Programs.
- The KSC Beachside Corrosion Test Site was established at that time to conduct controlled corrosion studies for corrosion protective coatings.

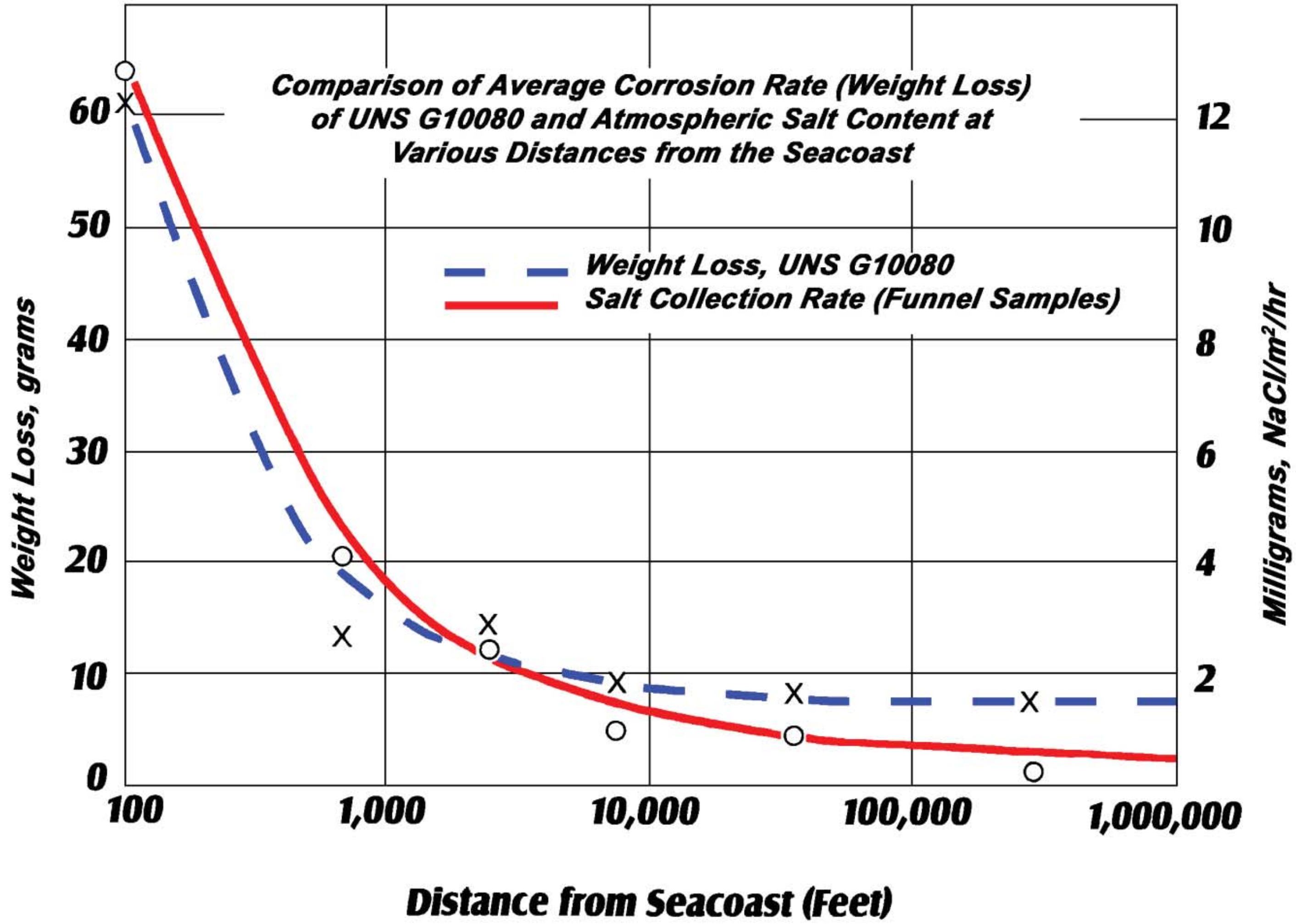


Saturn V

# KSC Beachside Corrosion Test Site

# Coupon Exposure Stands

# Changes in Corrosion Rate with Distance from the Ocean



# Corrosion Rates of Carbon Steel

| Corrosion rates of carbon steel calibrating specimens at various locations* | | | |
|---|---|---|---|
| Location | Type Of Environment | µm/yr | Corrosion rate[a] mils/yr |
| Esquimalt, Vancouver Island, BC, Canada | Rural marine | 13 | 0.5 |
| Pittsburgh, PA | Industrial | 30 | 1.2 |
| Cleveland, OH | Industrial | 38 | 1.5 |
| Limon Bay, Panama, CZ | Tropical marine | 61 | 2.4 |
| East Chicago, IL | Industrial | 84 | 3.3 |
| Brazos River, TX | Industrial marine | 94 | 3.7 |
| Daytona Beach, FL | Marine | 295 | 11.6 |
| Pont Reyes, CA | Marine | 500 | 19.7 |
| Kure Beach, NC (80 ft. from ocean) | Marine | 533 | 21.0 |
| Galeta Point Beach, Panama CZ | Marine | 686 | 27.0 |
| *Kennedy Space Center, FL (beach)* | *Marine* | *1070* | *42.0* |

[a]Two-year average
* Data extracted from: S. Coburn, Atmospheric Corrosion, in Metals Handbook, 9th ed, Vol. 1, Properties and Selection, Carbon Steels, American Society for Metals, Metals Park, Ohio, 1978, p.720



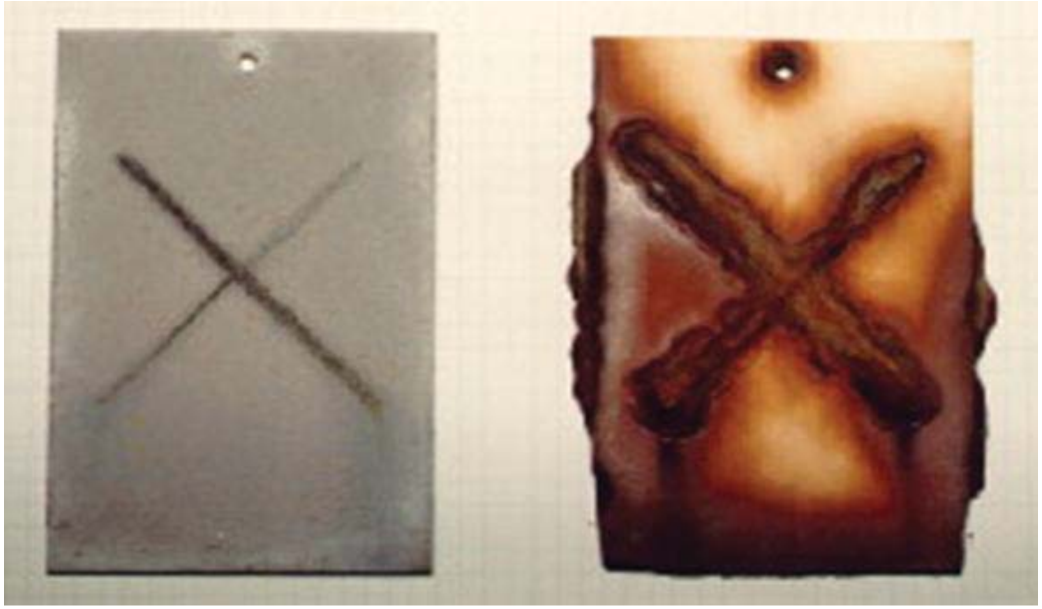
*A mil is one thousandth of an inch*

# KSC Atmospheric Corrosion Test Site

- **Documented by American Society for Metals (ASM) as one of the most corrosive naturally occurring environments in North America**
- **Actively maintained for more than 4 decades**
- **Historical database for evaluation of new materials**
- **On-site laboratory for real time atmospheric and seawater immersion corrosion investigation**
- **Remote access network connectivity for data acquisition and real time video by the Internet**
- **Instrumented for complete weather information**
- **Weather database from July 1995 available from Corrosion Technology Laboratory Website: [http://corrosion.ksc.nasa.gov/](http://corrosion.ksc.nasa.gov/)**

# History

- **A 1969 Study determined that inorganic zinc-rich primers (ZRPs) outperformed organic zinc in the KSC seacoast environment and that, in general, top-coats were detrimental to the long-term performance of the inorganic ZRPs.**
- **Some of the panels exposed at the Beach Site for this study are still in perfect condition.**



ZRP (without top-coat)    Epoxy and urethane coated ZRP

# History

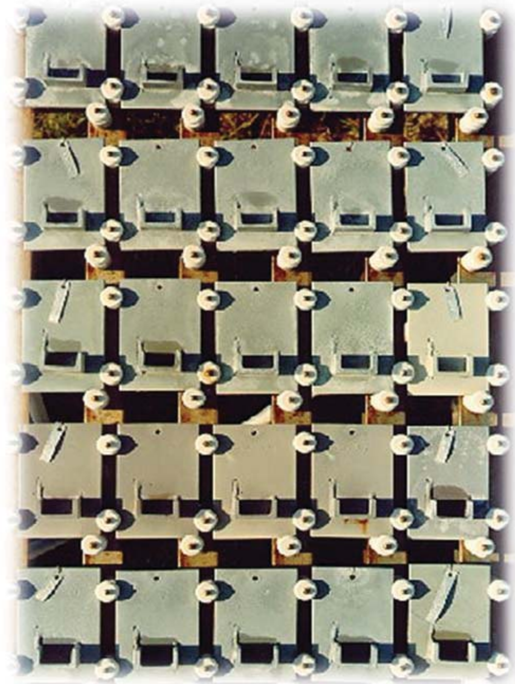
- In 1981 the Space Shuttle introduced acidic deposition problems to the ZRP coatings.
- Studies conducted to identify coating systems to improve the chemical resistance of zinc primers
- 10 topcoat systems were approved for use in the Space Shuttle launch environment.

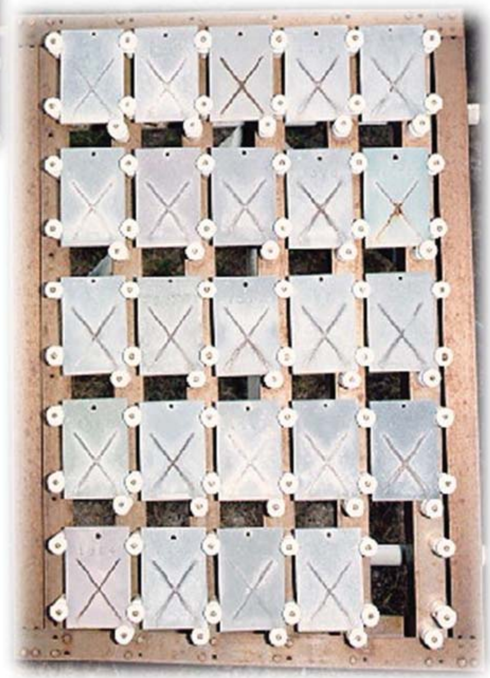
# History

- The coating systems selected were all solvent-based
- Clean Air legislation and environmental regulations began to restrict the use of solvents in paints
- A 1995 Study determined that a total inorganic coating systems provided excellent protection in launch environments

# Atmospheric Exposure

**Real world exposure at a site that mimics actual performance requirements**

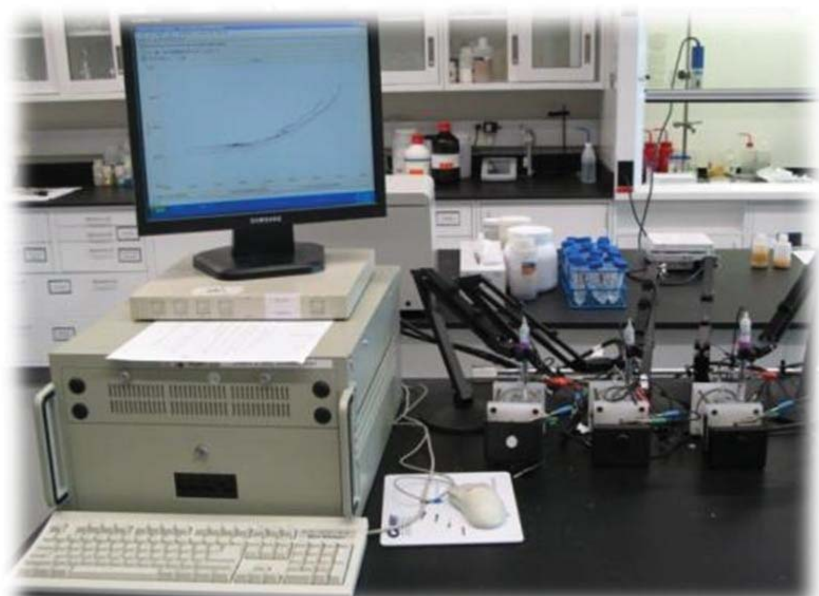




**NASA Technical Standard for Protective Coatings (NASA-STD-5008B) requires 18 months of good performance for preliminary approval and continued good performance for 5 years for final approval of a coating system.**

# Coatings Evaluation at KSC (current)

- **Application**
- **Weathering**
- **Appearance**
- **Standard Test Methods**
  - **ASTM Test Methods**
  - **ISO Test Methods**
  - **MIL Standards**
  - **Other Standards**

# Environmentally Driven Projects

- Environmentally Friendly Corrosion Protective Coatings for Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment
- Hexavalent Chrome Free Coatings
- Alternative to Nitric Acid Passivation
- Low VOC Topcoats for Thermal Spray Coatings
- Environmentally Friendly Corrosion Protective Compounds (CPCs)
- Smart and Multifunctional Corrosion Protective Coating Development

# Environmentally Friendly Corrosion Protective Coatings And Corrosion Preventative Compounds (CPCs)

- Progressively stricter environmental regulations are driving the coating industry to abolish many corrosion protective coatings and corrosion preventative compounds (CPCs) that are not environmentally friendly.

- The objective of these projects is to identify, test, and develop qualification criteria for environmentally friendly corrosion protective coatings and corrosion preventative compounds (CPCs) for flight hardware and ground support equipment .

**Dead tree/fish label warnings required in Europe for zinc primers**

**Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment**. (Europe MSDS))

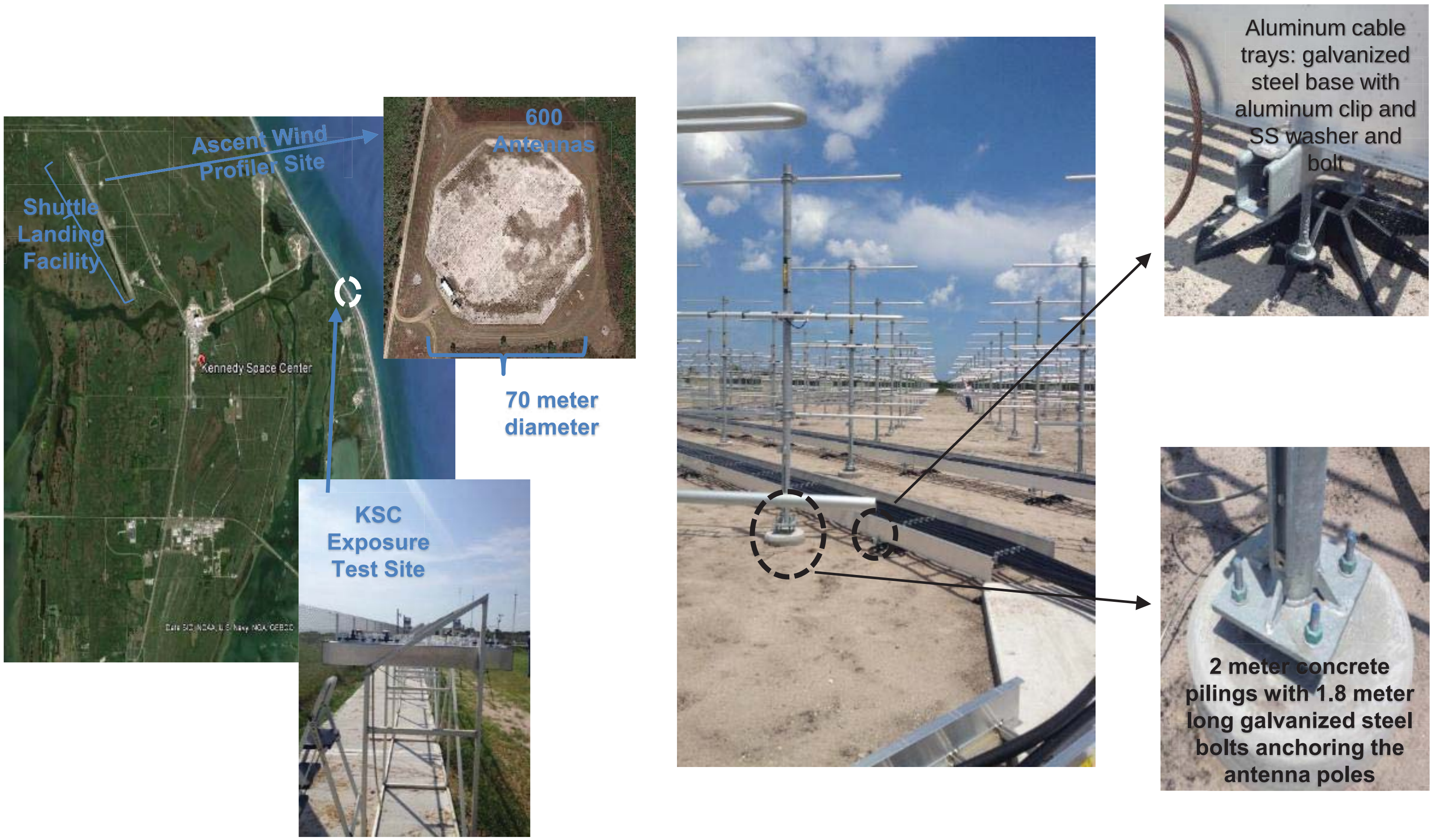
**Keep out of waterways**. (US MSDS)

# Corrosion Preventive Compounds (CPCs)

## Example: Ascent Wind Profiler, World's Largest Doppler Radar Site

## Located at the north side of the NASA KSC Shuttle Landing Facility

## Areas of Dissimilar Metal and Crevice Corrosion



# Alternative to Nitric Acid Passivation

**Expected Results**

- Provide the data necessary to verify that citric acid can be used as an environmentally preferable alternative to nitric acid for passivation of stainless steel

**Benefits of Citric Acid**

- Citric acid does not remove nickel, chromium, and other heavy metals from alloy surfaces
- Reduced risk associated with worker health and safety
- Reduced hazardous waste generation resulting in reduced waste disposal costs
- Reduced Nitrogen Oxide (NOx) emissions that are a greenhouse gas, contribute to acid rain and smog, and increased nitrogen loading (oxygen depletion) in bodies of water

Image: Master isolated images / FreeDigitalPhotos.net

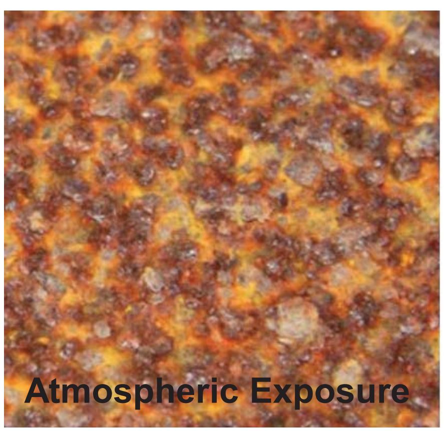
# Technology Development

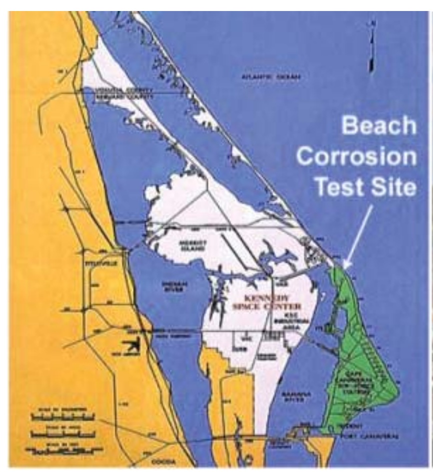
- Long-term prediction of corrosion performance from accelerated tests.
- Coating development (Smart coatings for corrosion detection and control).
- Detection of hidden corrosion.
- Self-healing coatings.

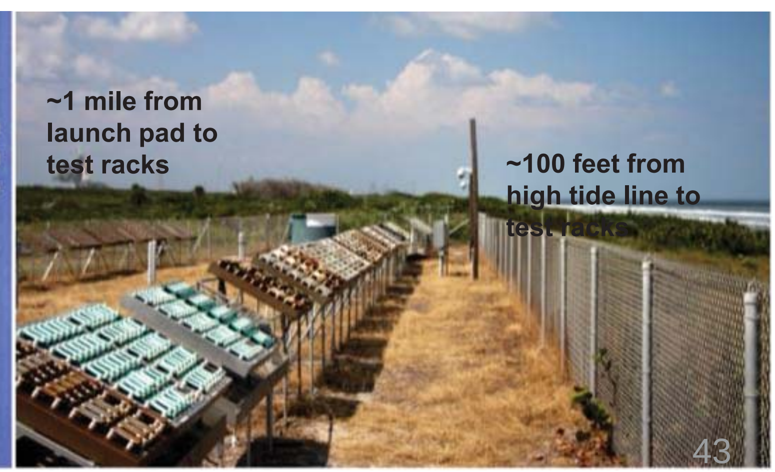
**1010 steel (UNS 10100) panels after prolonged exposure**



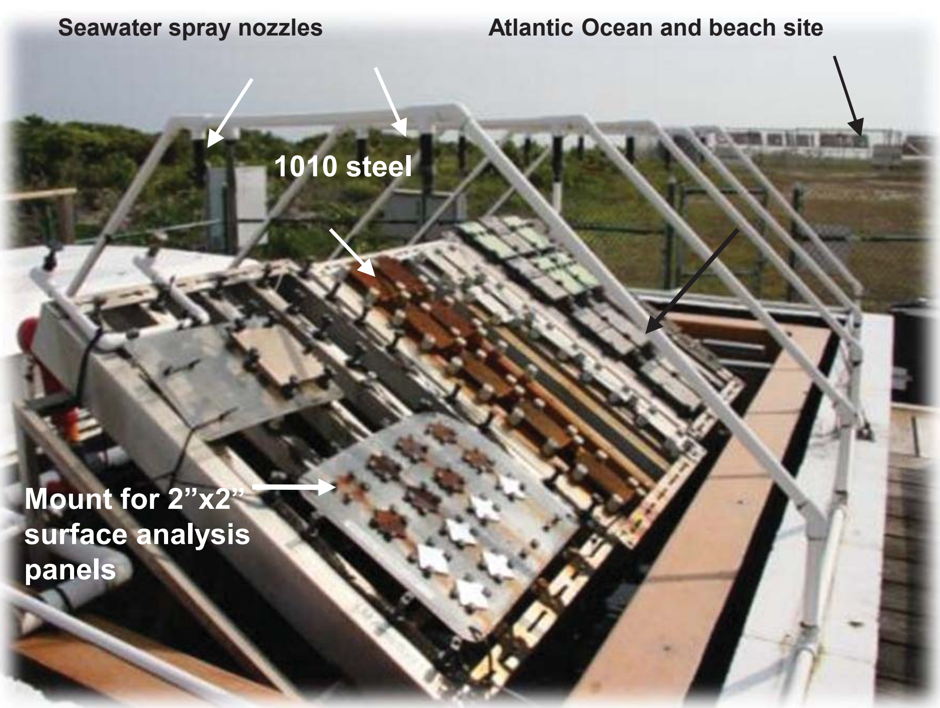
Correlation?



# Timescale Correlation between Marine Atmospheric Exposure and Accelerated Corrosion Testing



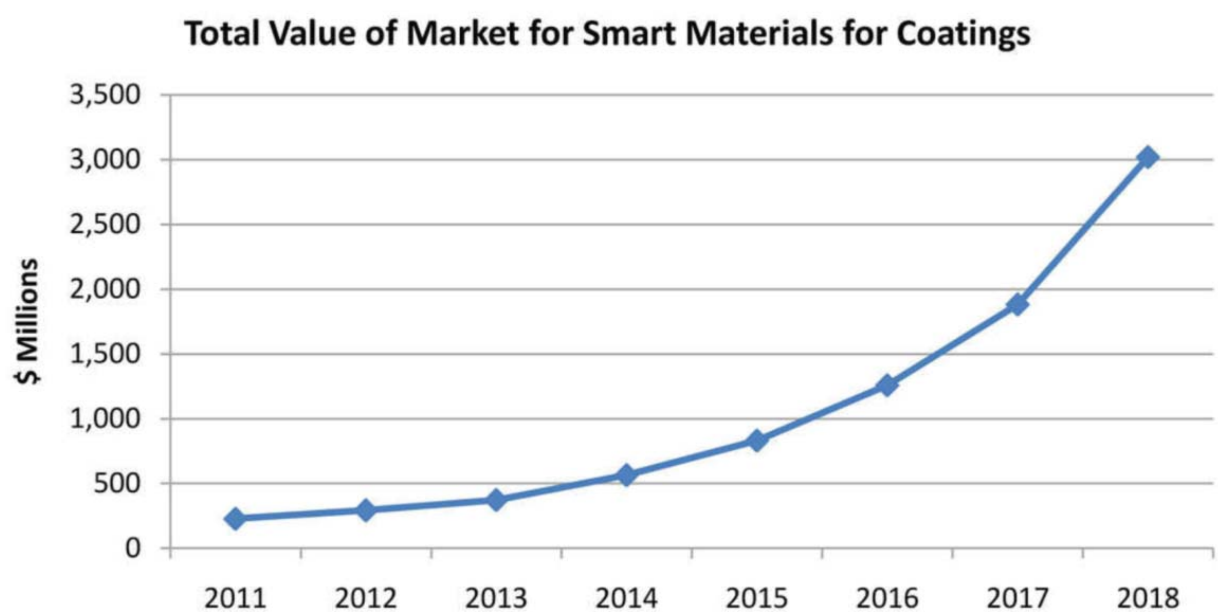


**Alternating Seawater Spray System with exposure panels, and modification for panels used for surface analysis (left). Wet candles exposed to KSC beachside atmospheric conditions and used to measure chloride concentration per month (right).**

# Corrosion Protective Coatings

- Barrier (passive)
- Barrier plus corrosion inhibiting components:
  - Sacrificial (zinc-rich primers)
  - Corrosion inhibitors (can have detrimental effects on the coating properties and the environment; most expensive additive; subject to progressively stricter environmental regulations)
- Smart (active)

The market for smart coatings is forecasted to reach a size of USD 3 billion by 2018. Source: Nanomarkets, LC.



# Smart Coatings for Corrosion Control

- The use of "smart coatings" for corrosion sensing and control relies on the changes that occur when a material degrades as a result of its interaction with a corrosive environment.
- Such transformations can be used for detecting and repairing corrosion damage.
- NASA is developing a coating that can detect and repair corrosion at an early stage.
- This coating is being developed using pH-sensitive microcontainers that deliver their contents when corrosion starts to:
  - Detect and indicate the corrosion location
  - Deliver environmentally friendly corrosion inhibitors
  - Deliver healing agents to repair mechanical coating damage.

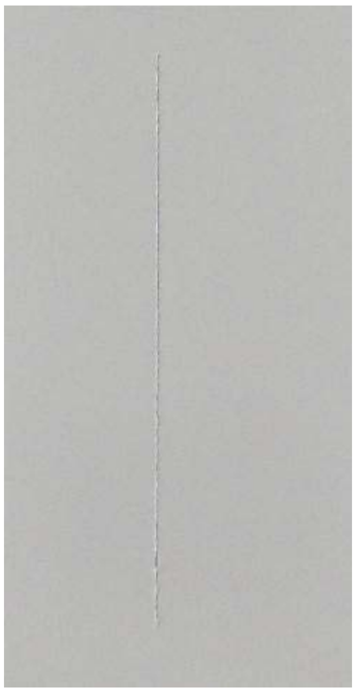
http://upload.wikimedia.org/wikipedia/commons/1/12/Cape_Dwarf_Chameleon.jpg

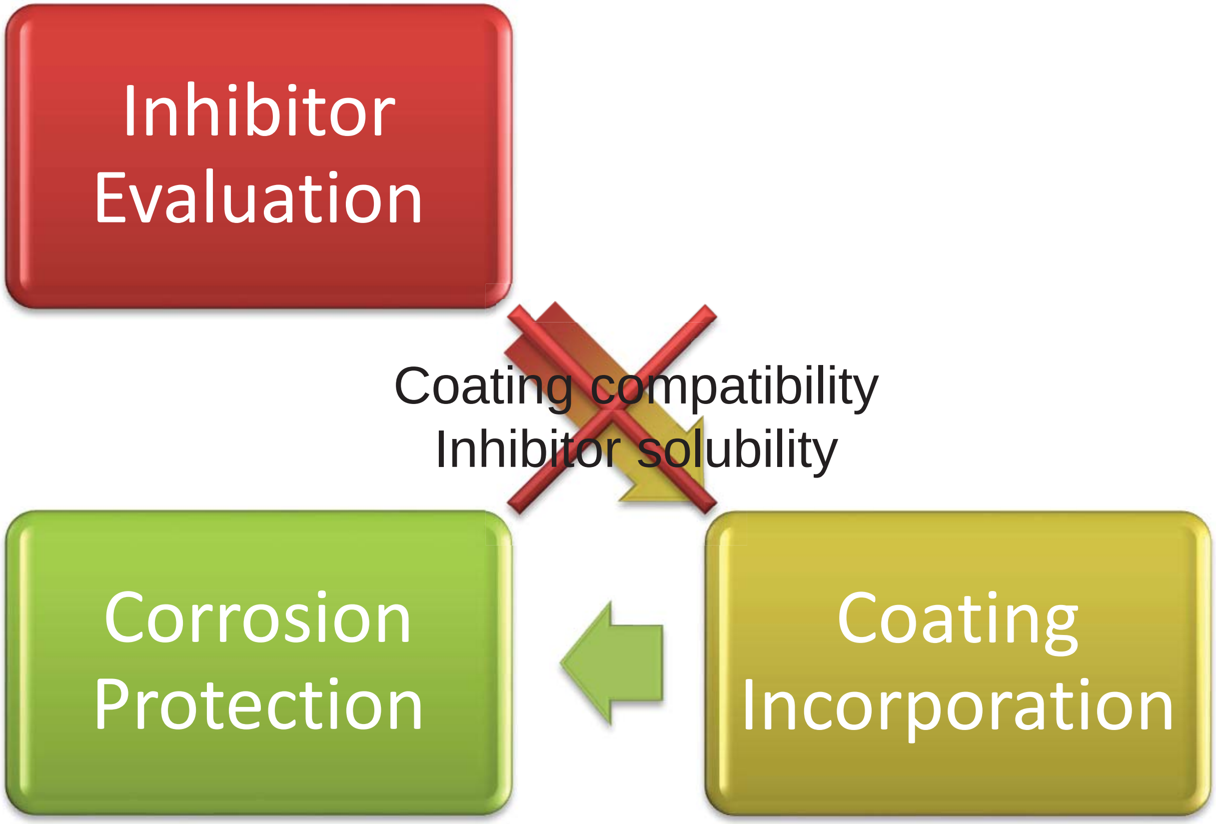
# Feedback-Active Microcontainers for Corrosion Detection and Control

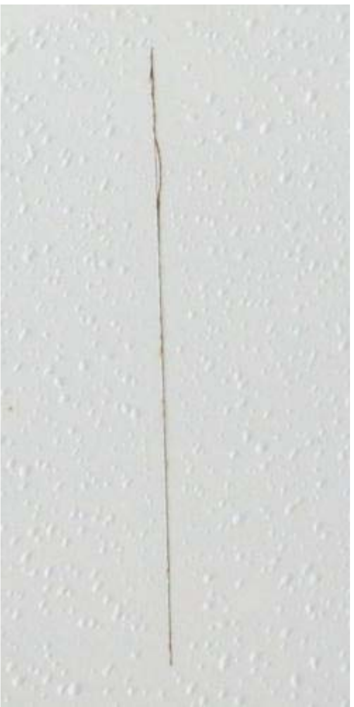
- Containers with an active ingredient-rich core and stimuli-responsive shell (microcapsules)
- Containers with an active ingredient incorporated into a stimuli-responsive matrix (microparticles)
- Containers with a porous ceramic core impregnated by inhibitor and enveloped by a stimuli-responsive polyelectrolyte (PE) shell*


*D. Grigoriev, D. Akcakayiran, M. Schenderlein, and D. Shcukin, Corrosion, 70 (2014): p.446-463.47

# Delivery System





# Electrochemical Nature of Corrosion

**Metal is oxidized (anodic reaction); something else is reduced (cathodic reaction)**

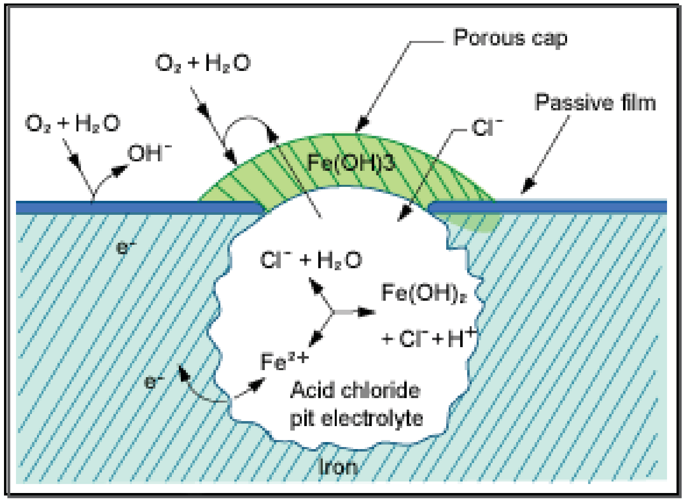
## Overall Reaction:

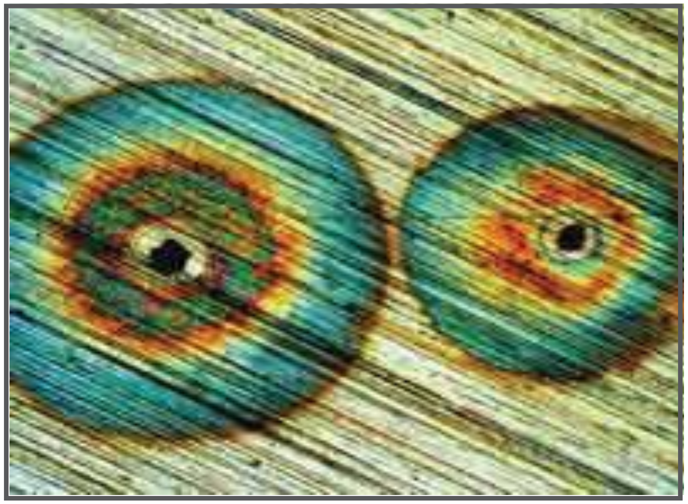
$$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

**Anodic:** $Fe \rightarrow Fe^{2+} + 2e^-$

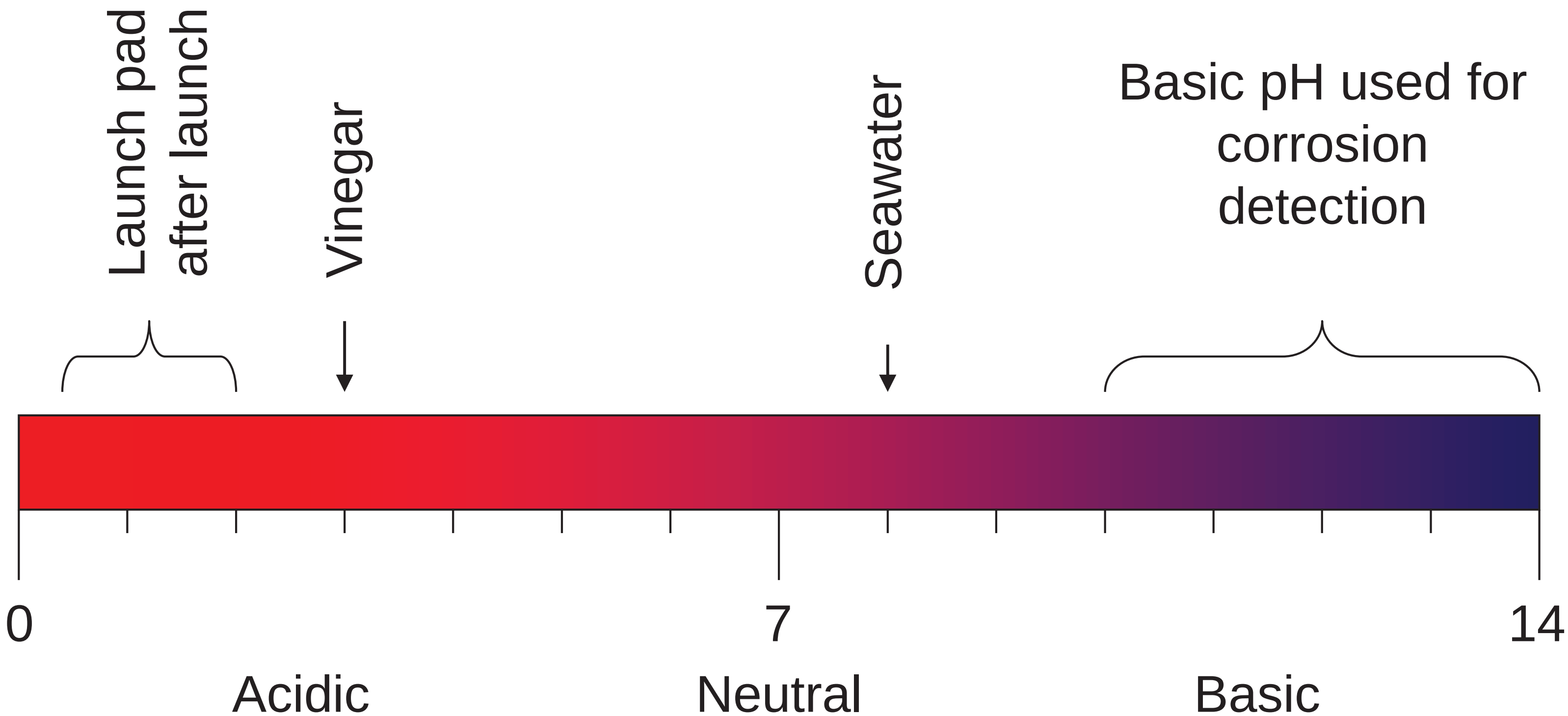
## Cathodic:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$



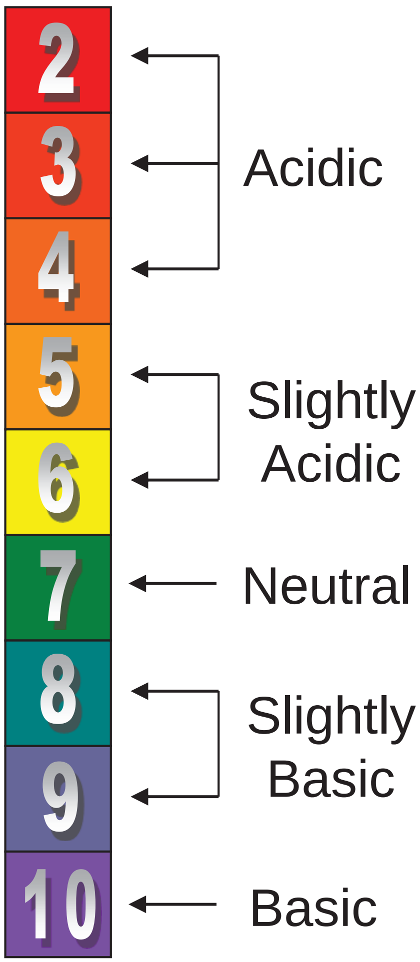
# Corrosion and pH

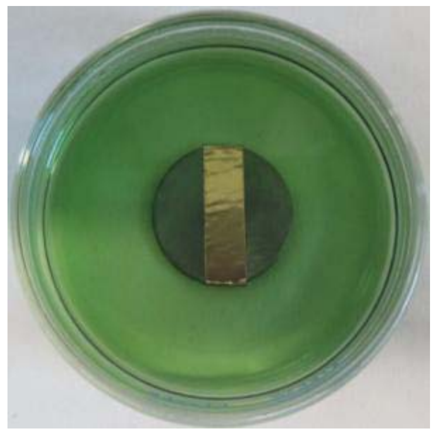



pH Scale

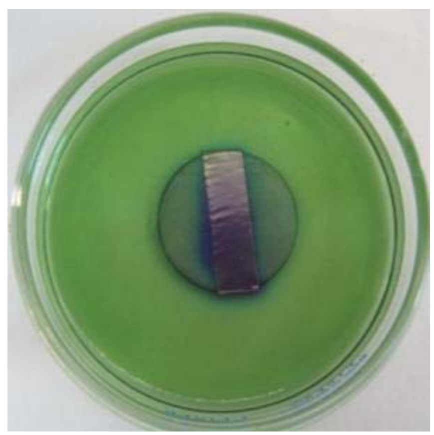
# Corrosion Indication

**pH changes that occur during corrosion of a metal**

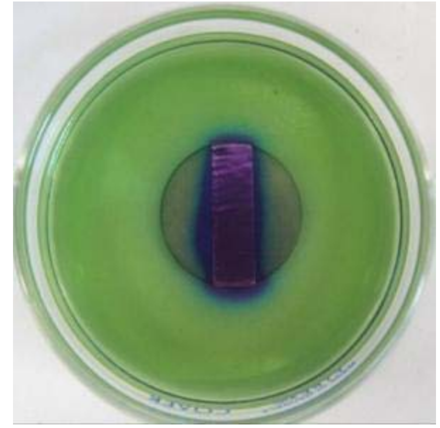


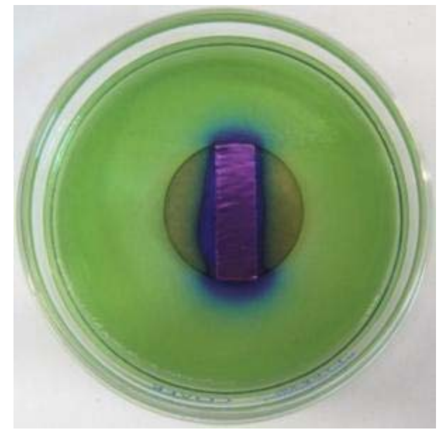
Elapsed Time: 0 hours



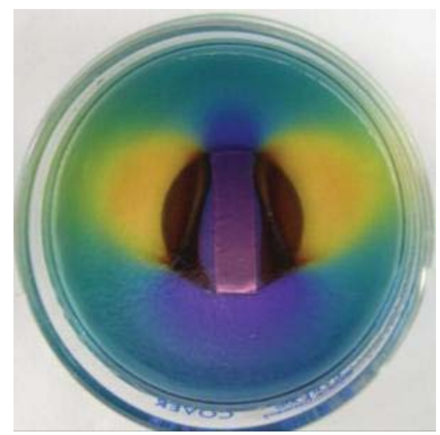
0.5 hours



1.5 hours

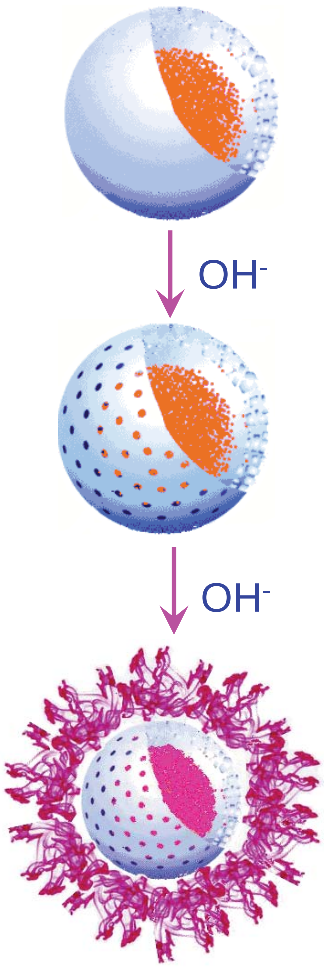


4.5 hours



3 days

# pH-triggered Release Microcapsules




**Microcapsule containing pH indicator (inhibitor, self healing agents)**

**The shell of the microcapsule breaks down under basic pH (corrosion) conditions**

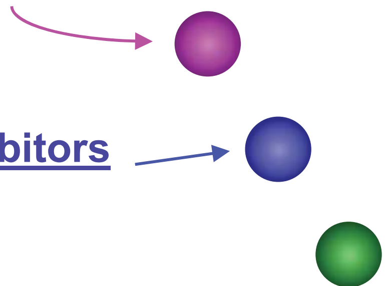
**pH indicator changes color and is released from the microcapsule when corrosion starts**

# Smart Coating Response to Corrosion and Mechanical Damage

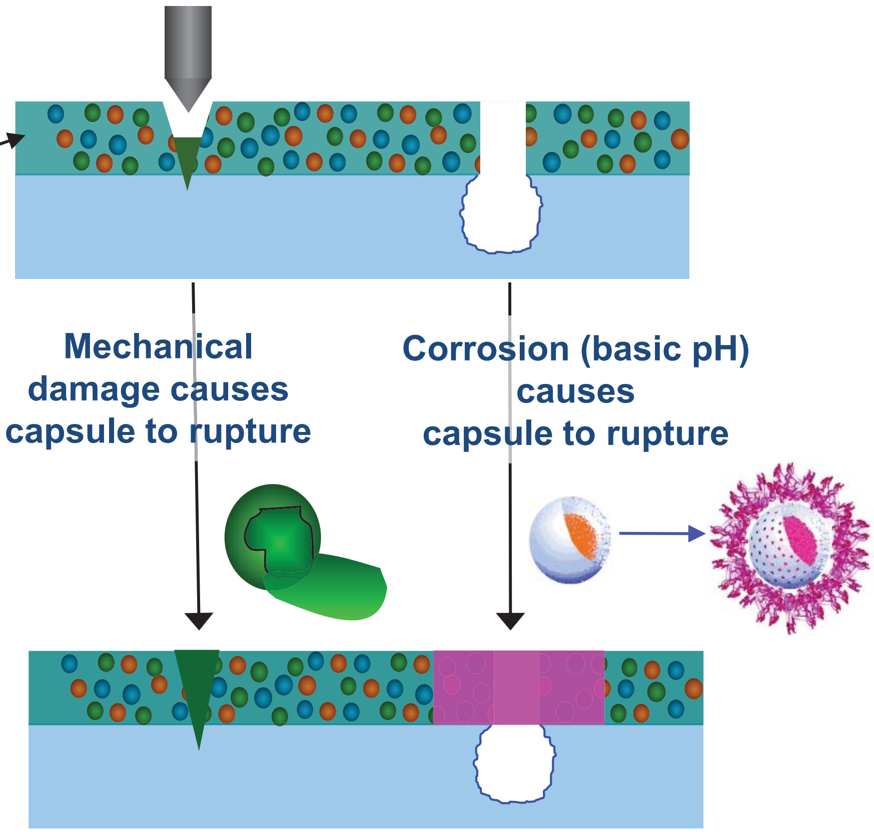
Corrosion indicators

Corrosion inhibitors

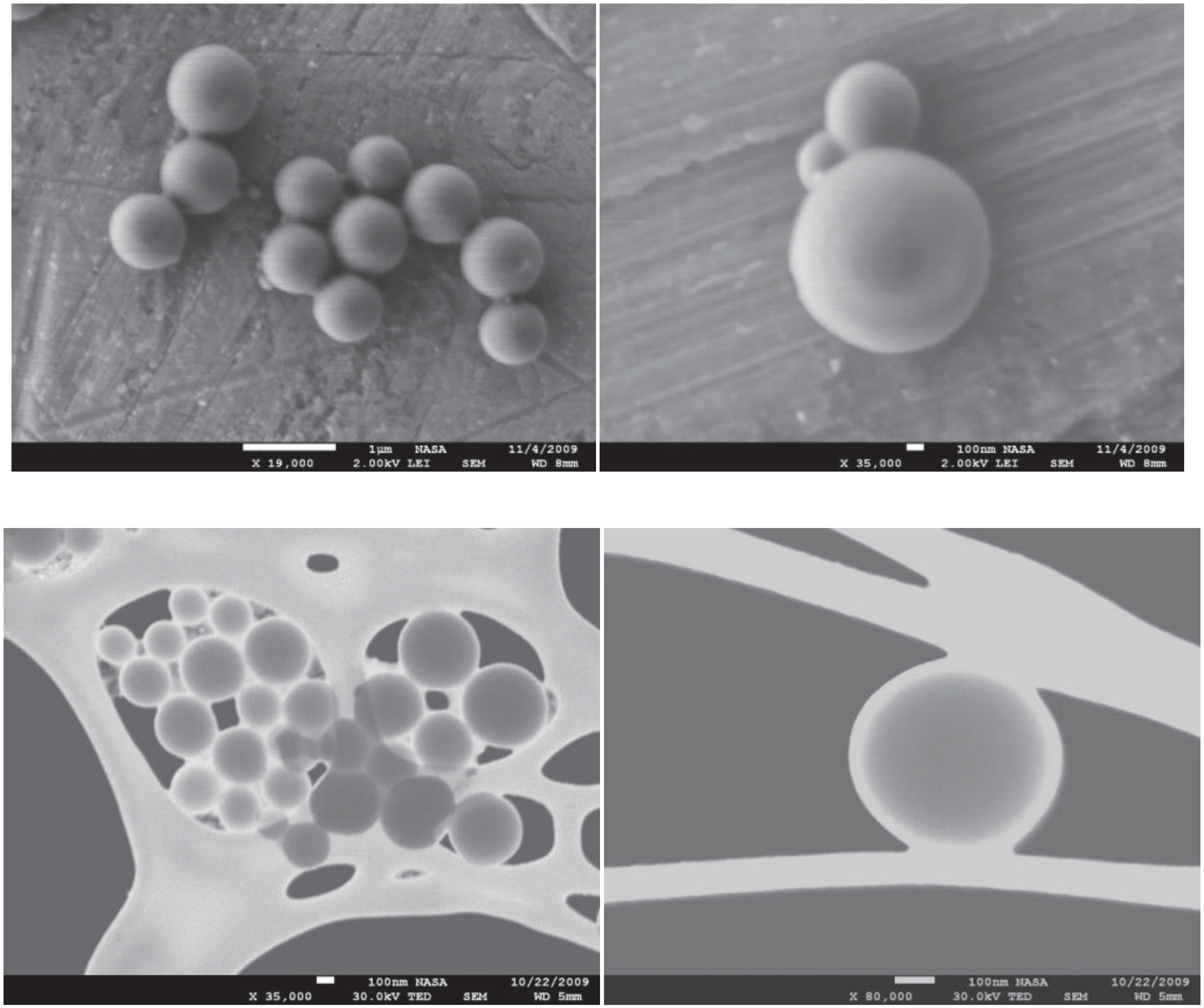
Self-healing agents



Microcapsules are incorporated into smart coating

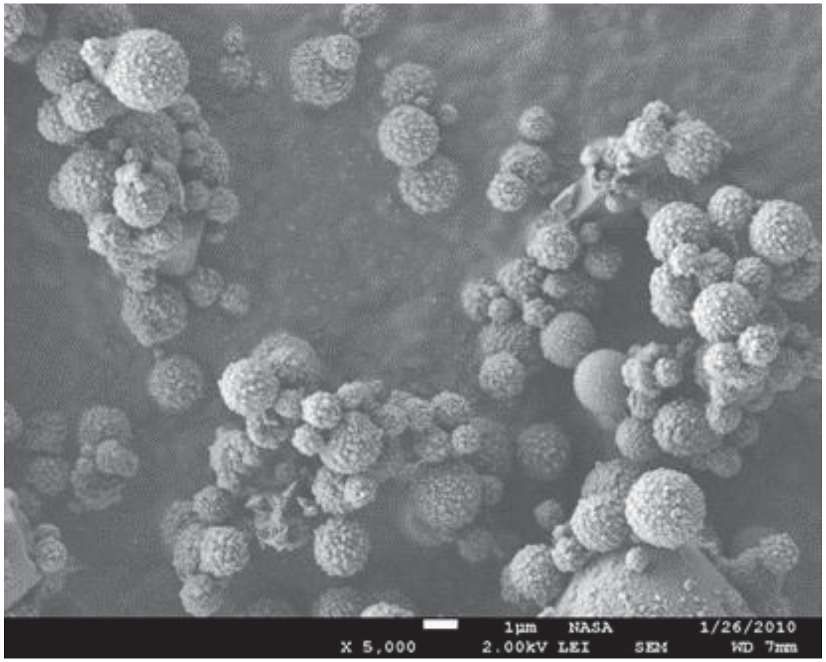


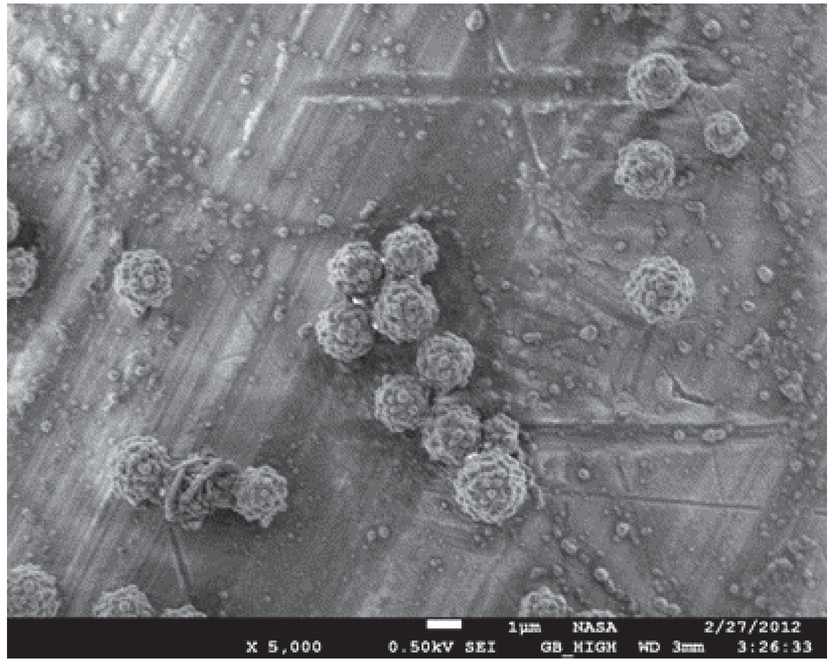

# Hydrophilic-core Microcapsules




SEM images of hydrophilic-core microcapsules

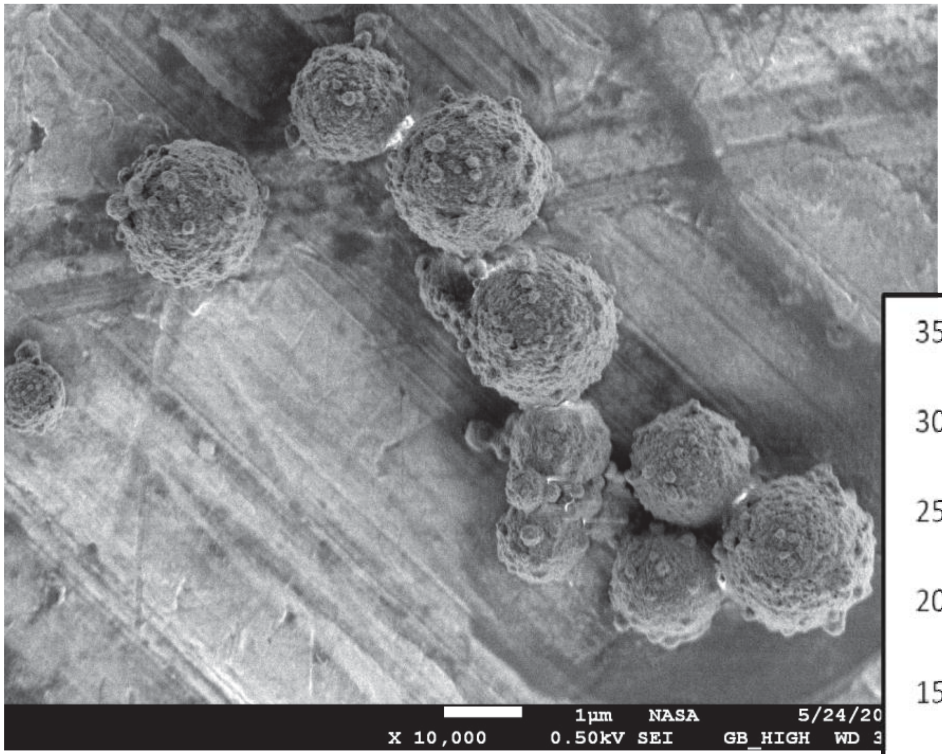
# Corrosion Indicating Microparticles

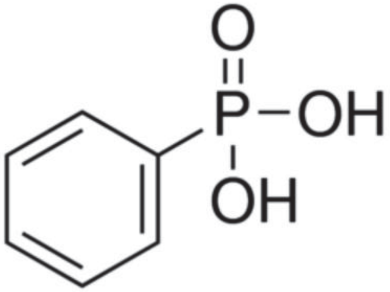


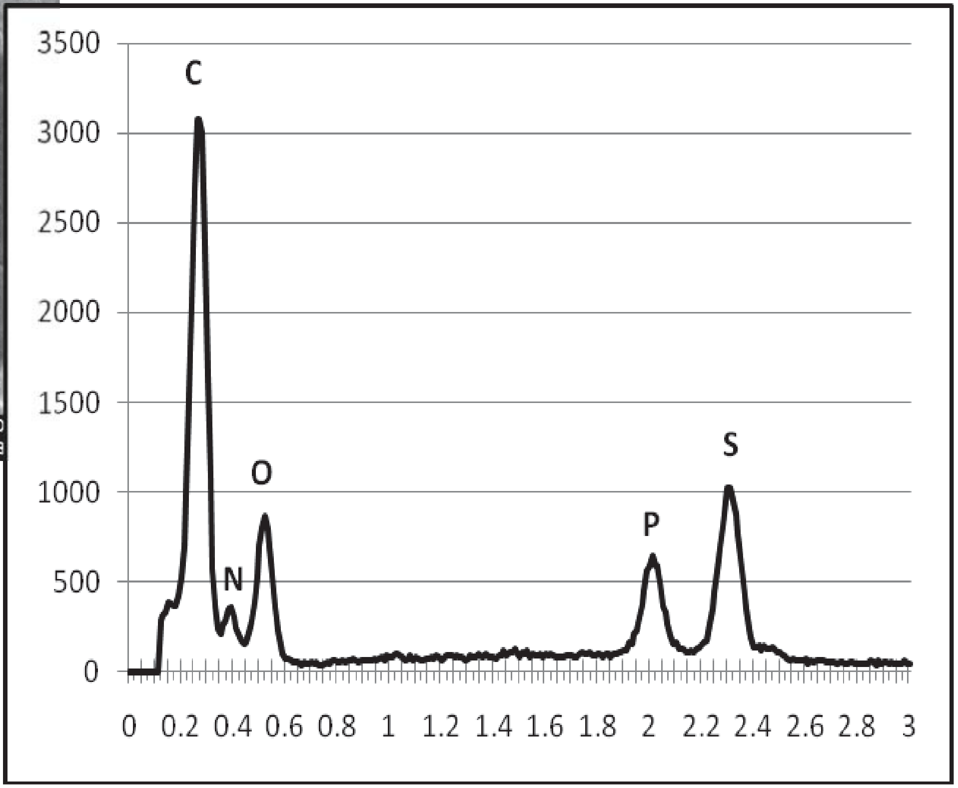




SEM image of microparticles with color changing indicator (left) and with fluorescent indicator (right)

# Microparticles with Inhibitors

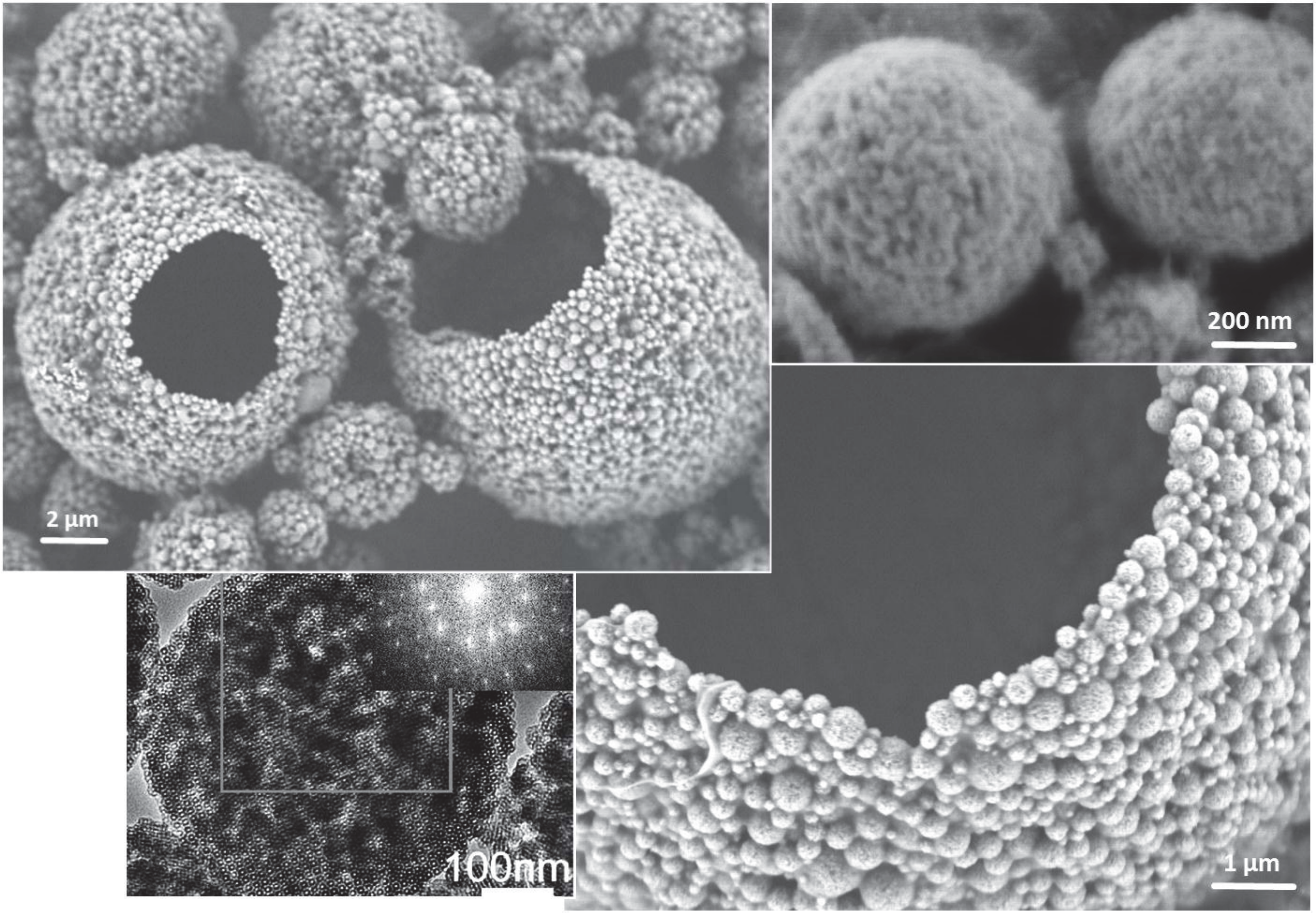


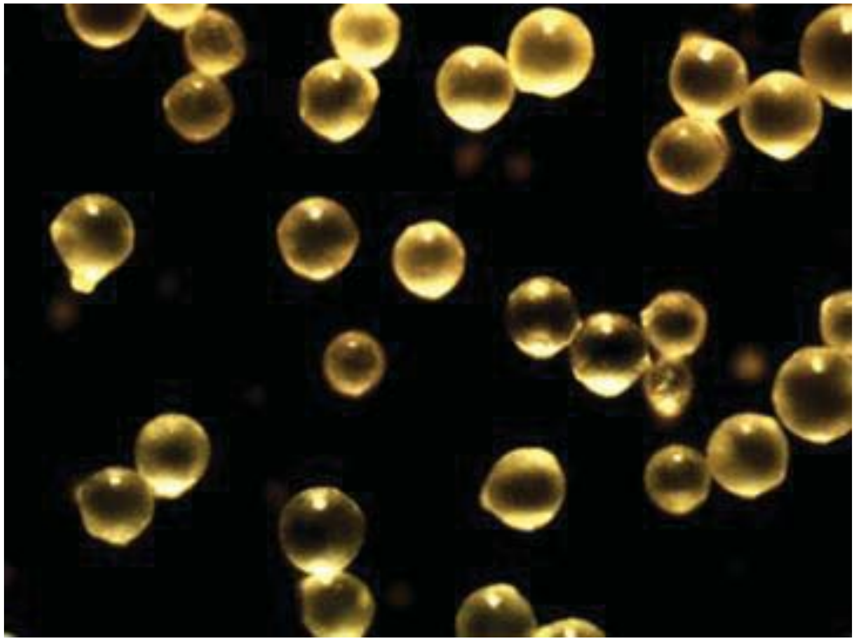



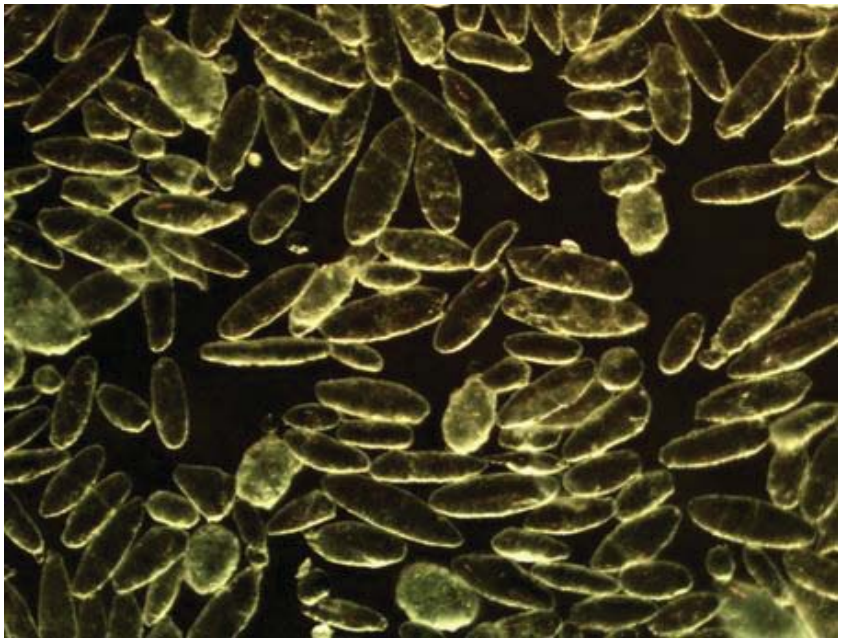

**SEM and EDS of microparticles with corrosion inhibitor phenylphosphonic acid (PPA)**

# Inorganic Carriers



# Microcapsules for Self-Healing Coatings



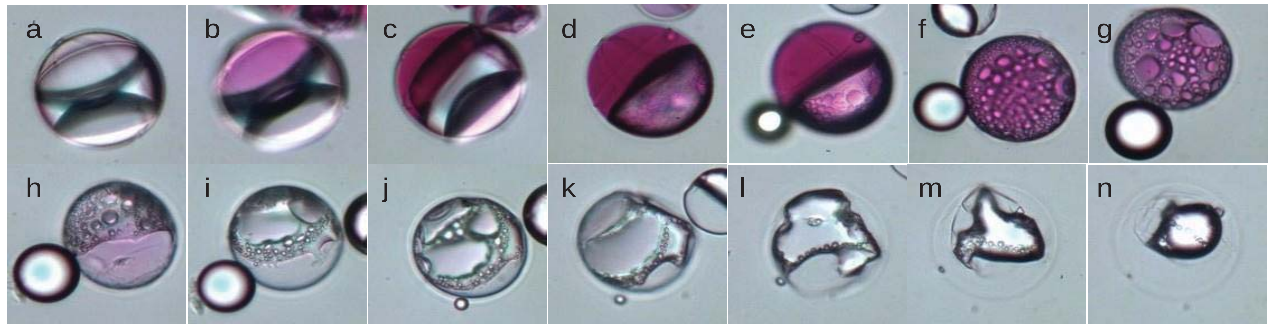


**Optical micrographs of spherical and elongated microcapsules for self-healing of mechanical scratches**

# Microcapsule Response to pH Increase

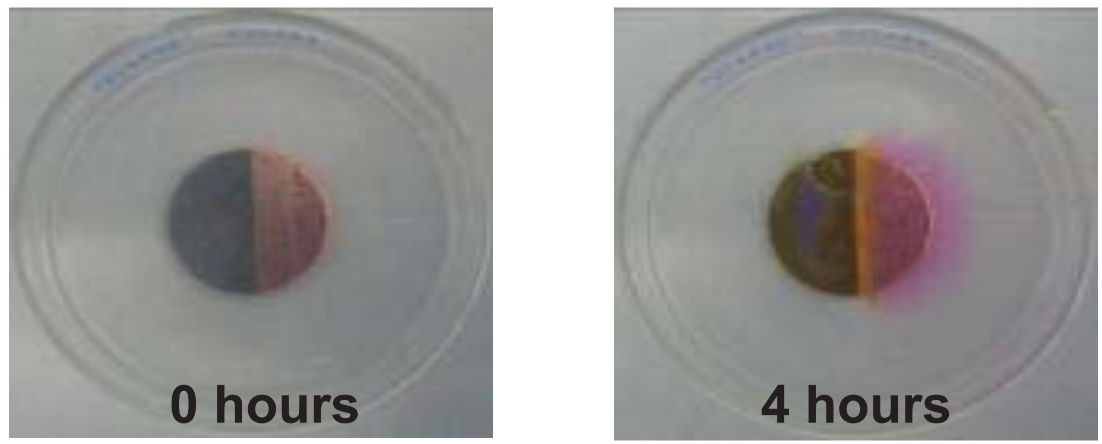
# Microcapsules for Corrosion Indication

pH sensitive microcapsules with corrosion indicator for corrosion detection




Time lapse pictures of a microcapsule with indicator breaking down under basic pH conditions.

**Significance:**
Damage responsive coatings provide visual indication of corrosion in hard to maintain/inaccessible areas (on towers) prior to failure of structural elements.

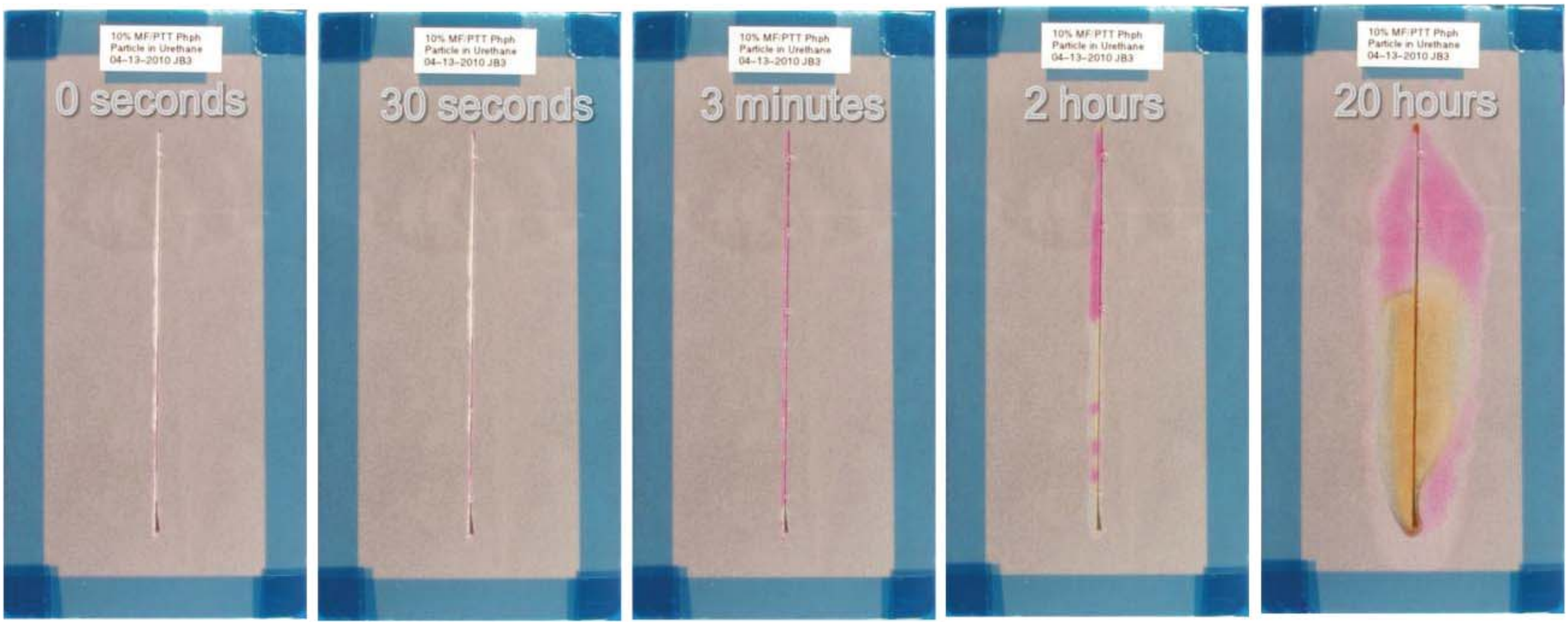



A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was immersed in gel with microcapsules containing a corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and progress of corrosion

# Early Indication of Corrosion

Early
indication
of
corrosion

# Experimental Corrosion Indicating Coating



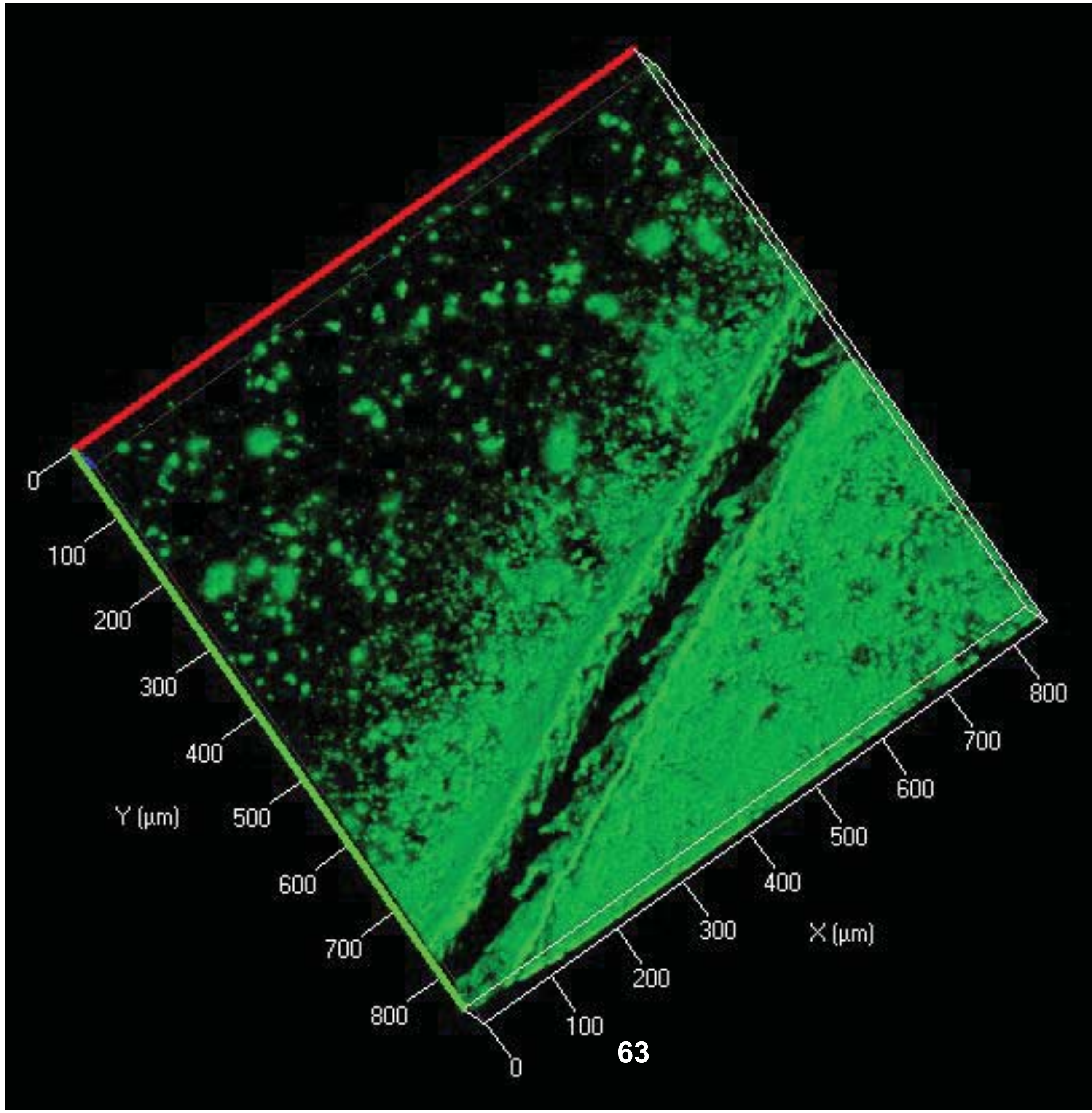

Salt fog test[1] results of panels coated with a clear polyurethane coating loaded with 20% oil core microcapsules with corrosion indicator in their core. The coating detects corrosion in the scribed area at a very early stage (0 seconds) before the appearance of rust is visible.

[1]ASTM B 117-97, Standard Practice for Operating Salt Spray (Fog) Apparatus,

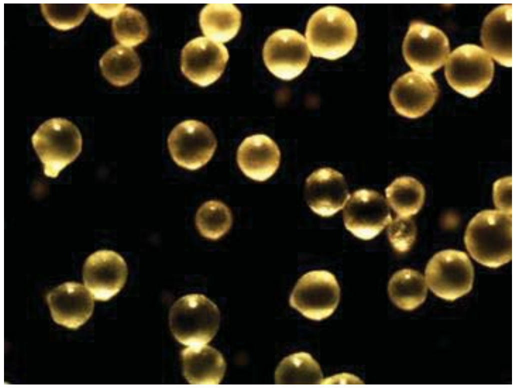
# Corrosion Indicating Microparticles in Coating

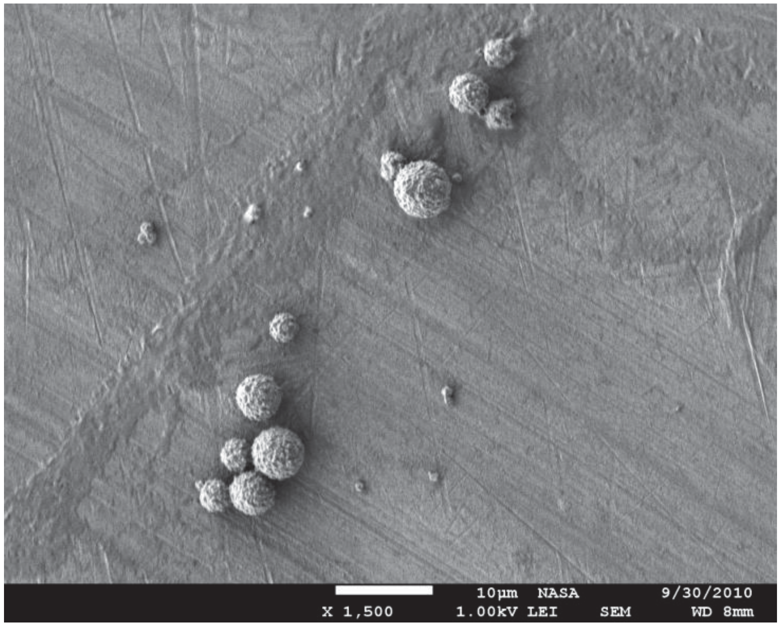

**Master Gain 446**

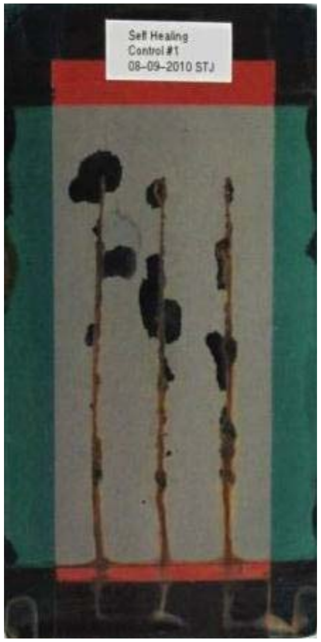
| | |
|---|---|
| Scaling X | 0.791 µm |
| Scaling Y | 0.791 µm |
| Scaling Z | 5.117 µm |
| Dimensions | x: 512, y: 512, z: 12, 8-bit |
| Image size | x: 404.06 µm, y: 404.06 µm, z: 56.29 µm |
| Scan Mode | stack |
| Zoom | 2.1 |
| Objective | EC Epiplan-Apochromat 10x/0.3 HD DIC M27 |
| Pixel dwell | 1.58 µs |
| Average | 1 |
| Master gain | 446 |
| Digital gain | 1.24 |
| Digital offset | 0.00 |
| Pinhole | 45 µm |
| Filters | 493 - 625 |
| Beam splitters | MBS : MBS 488<br>MBS_InVis : Plate |
| Lasers | 488 nm : 2.0 % |



# Self-Healing

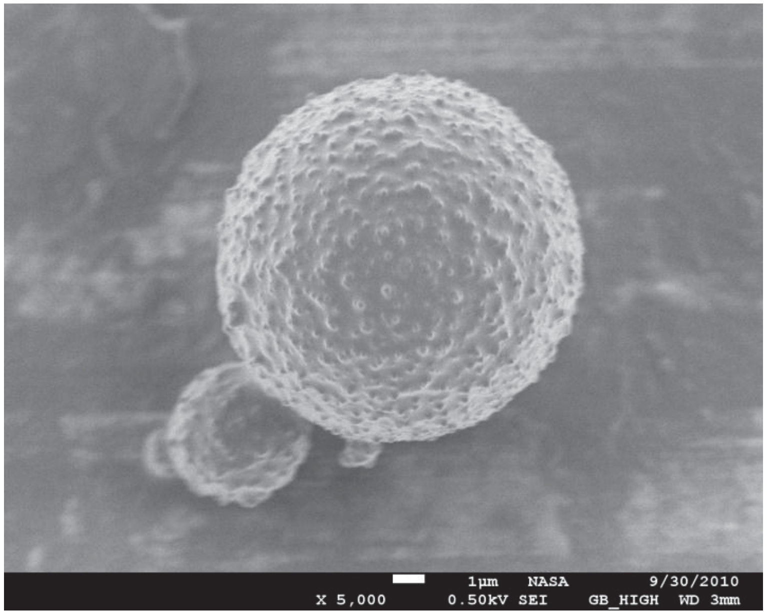






Siloxane microcapsules synthesized by *in situ* polymerization reaction procedure




Control and 2-Part siloxane capsule system (siloxane and tin catalyst), blended into an epoxy primer coating, after 700 hrs of salt fog exposure testing. Coating thickness is about 400µm and microcapsule content is 20 wt%.

# Summary

- KSC is located in one of the most naturally corrosive areas in North America.
- Acidic exhaust from SRBs exacerbate natural corrosive conditions at the launch pads.
- NASA has encountered numerous environmentally driven challenges in corrosion protection since the inception of the Space Program.
- NASA is engaged in projects aimed at identifying more environmentally friendly and sustainable corrosion protection coatings and technologies.
- Current technology development efforts target the development of smart coatings for corrosion detection and control and the development of a new accelerated corrosion test method that correlates with long-term corrosion test methods.
- Website: [http://corrosion.ksc.nasa.gov/](http://corrosion.ksc.nasa.gov/)

# Additional Information

Corrosion Technology Laboratory

Search | Site Map

Kennedy Space Center

Home | Facilities | Coatings | Corrosion Fundamentals | Resources | Customers | KSC Home Page

The Corrosion Technology Laboratory at the NASA Kennedy Space Center is a network of capabilities – people, equipment, and facilities that provide technical innovations and engineering services in all areas of corrosion for NASA and external customers.

*The Corrosion Technology Laboratory:*

- Provides consulting and testing services for NASA and external customers
- Conducts applied research
- Develops new corrosion detection and control technologies
- Investigates, evaluates, and determines materials performance and degradation in different environments in support of NASA, other government organizations, industry, and educational institutions
- Participates in educational outreach activities

**Introduction**

The cost of corrosion to the U.S.A. is $276 billion/year. This cost includes direct and indirect expenses associated with corrosion. This corrosion web site was developed to inform and educate the public on issues involving environmental deterioration of materials. Information and pictures of the corrosion engineering, research, and testing capabilities at the Kennedy Space Center (KSC) are presented. This virtual tour includes visits to the Corrosion Laboratory, Beachside Atmospheric Test Facility, Coating Application Laboratory, Accelerated Corrosion Laboratory, and Photo documentation Facilities. An educational look at the various forms of corrosion, with accompanying photography is provided. Technical and scientific publications are made available. Access is provided to a printable brochure about our KSC



**http://corrosion.ksc.nasa.gov/**

# NASA's Corrosion Technology Laboratory Team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*Thank you*